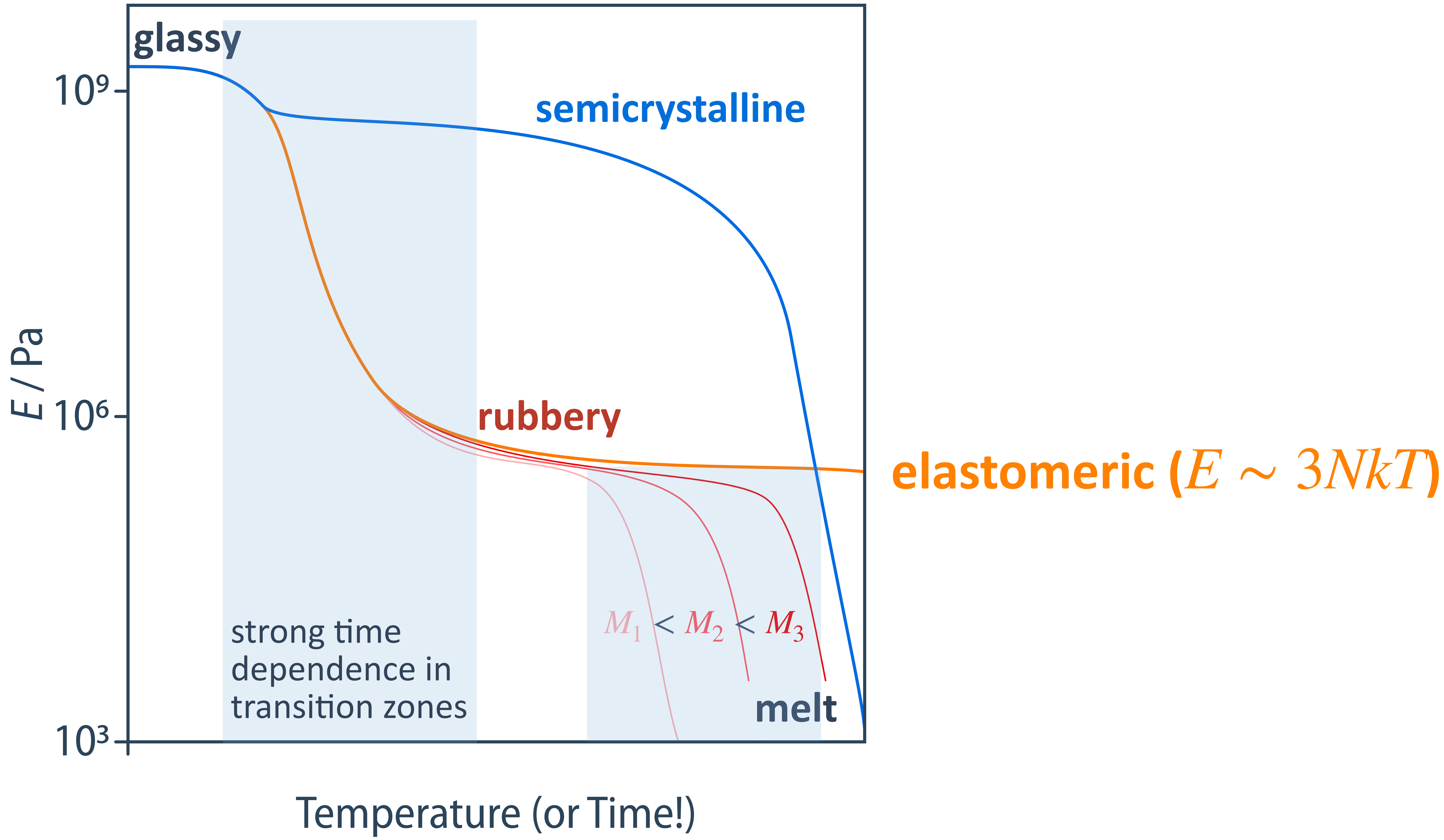
5.2
Viscoelasticity

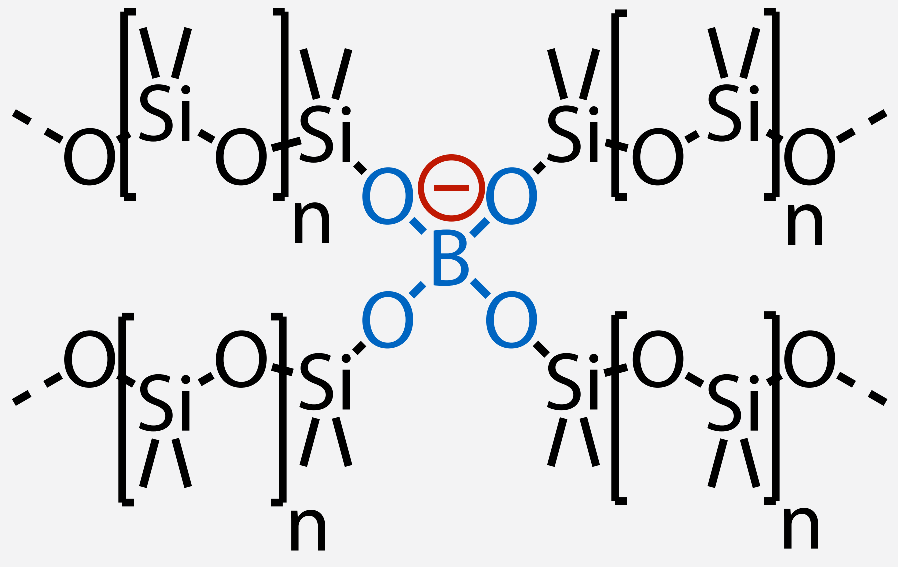
- **elastic solids (e.g. metals, ceramics) obey Hooke's law: $\sigma = E\epsilon$**
- elastic modulus is independent of time, t , and strain rate, $d\epsilon/dt$ (if T is not too high)



- **in contrast, polymer properties strongly influenced by t and $d\epsilon/dt$, particularly at around their transitions**

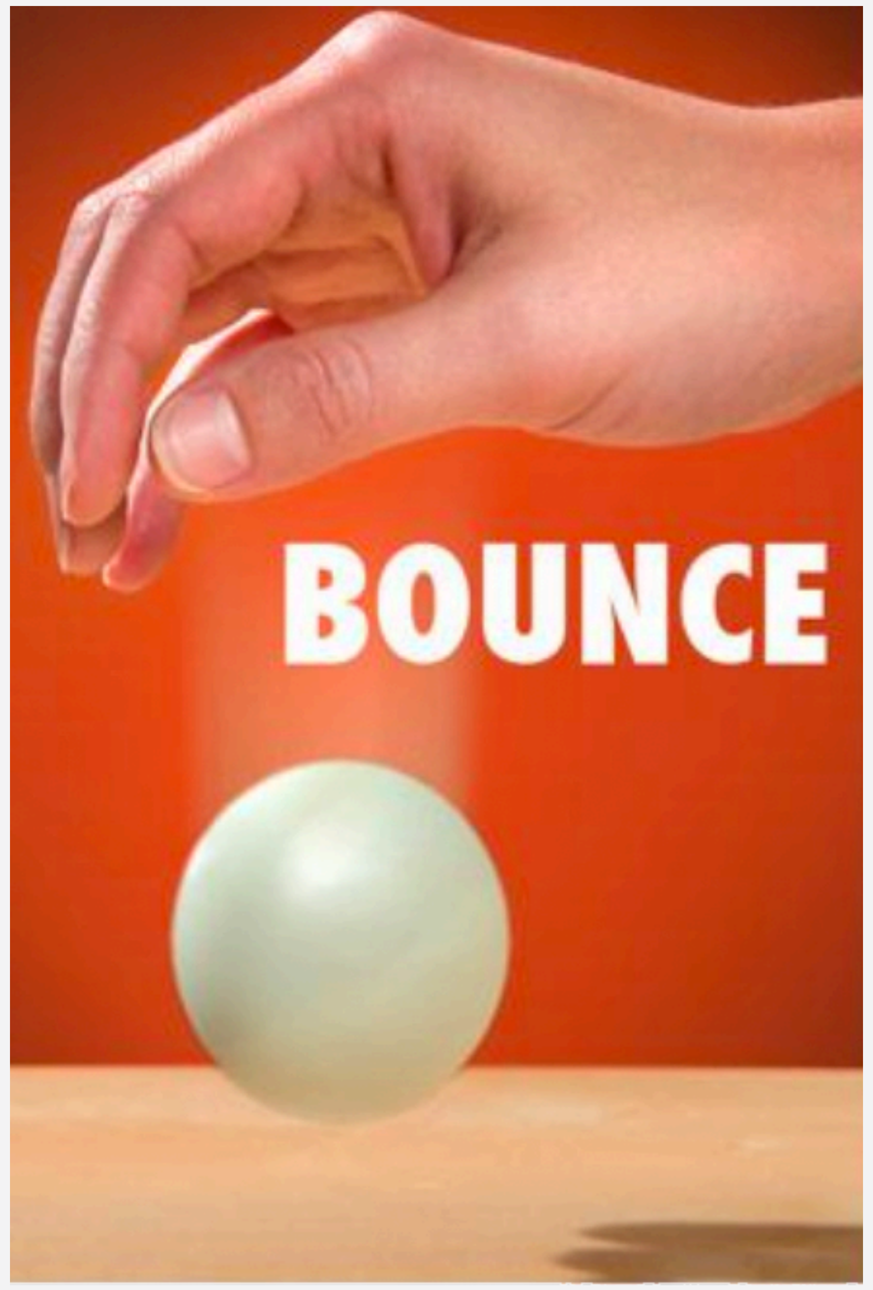
Example - Silly Putty

- transiently cross-linked poly(dimethoxysiloxane) (PDMS):



boronic ester
mediated cross-links

elastic solid



short time scales

deformability

“fast” strain rate

liquid flow

long time scales

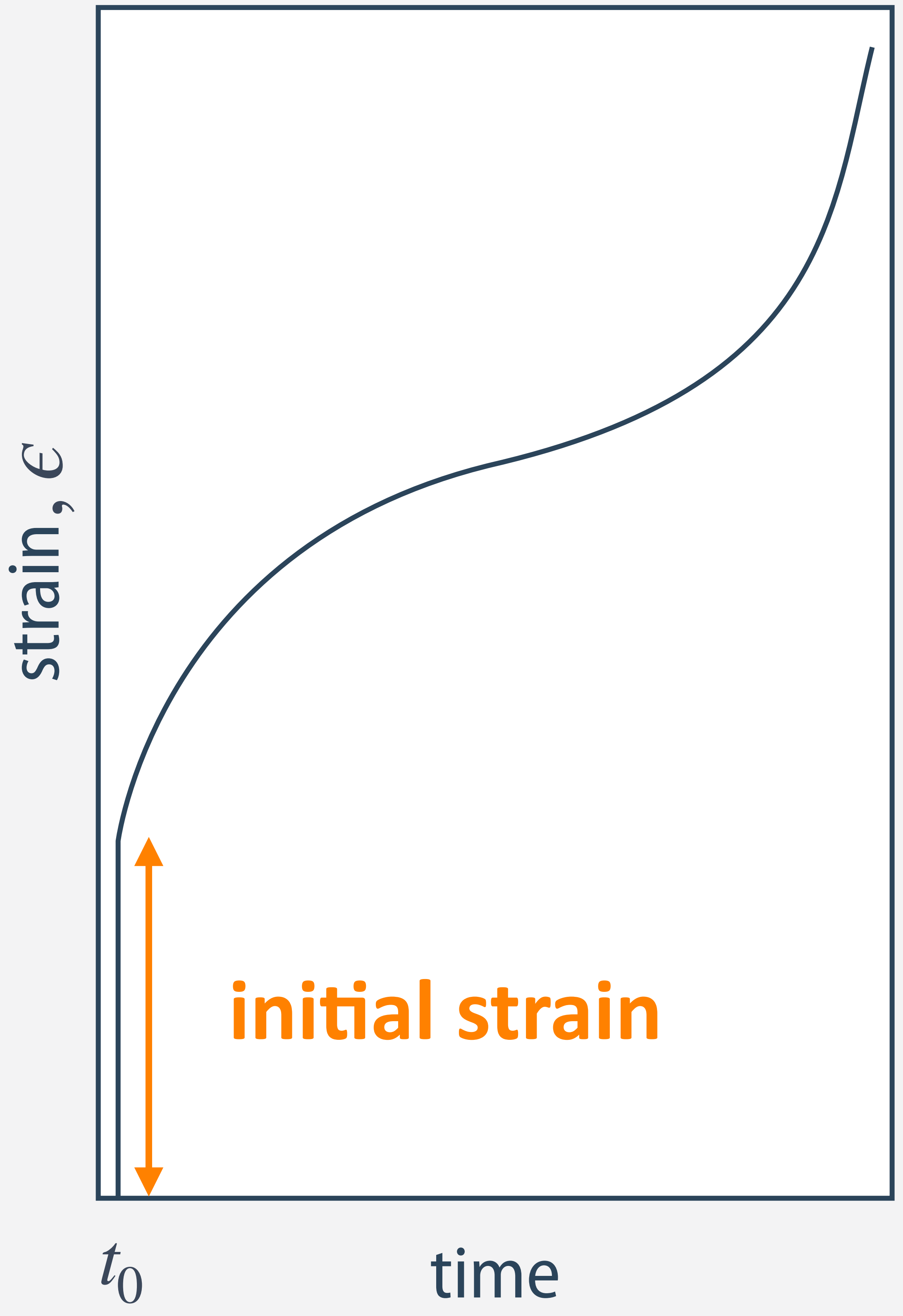
- **silly putty shows different mechanical properties depending on the time-scale**

Importance of Viscoelasticity

- **effect of time/frequency** and its **relation with temperature** determine technologically relevant properties

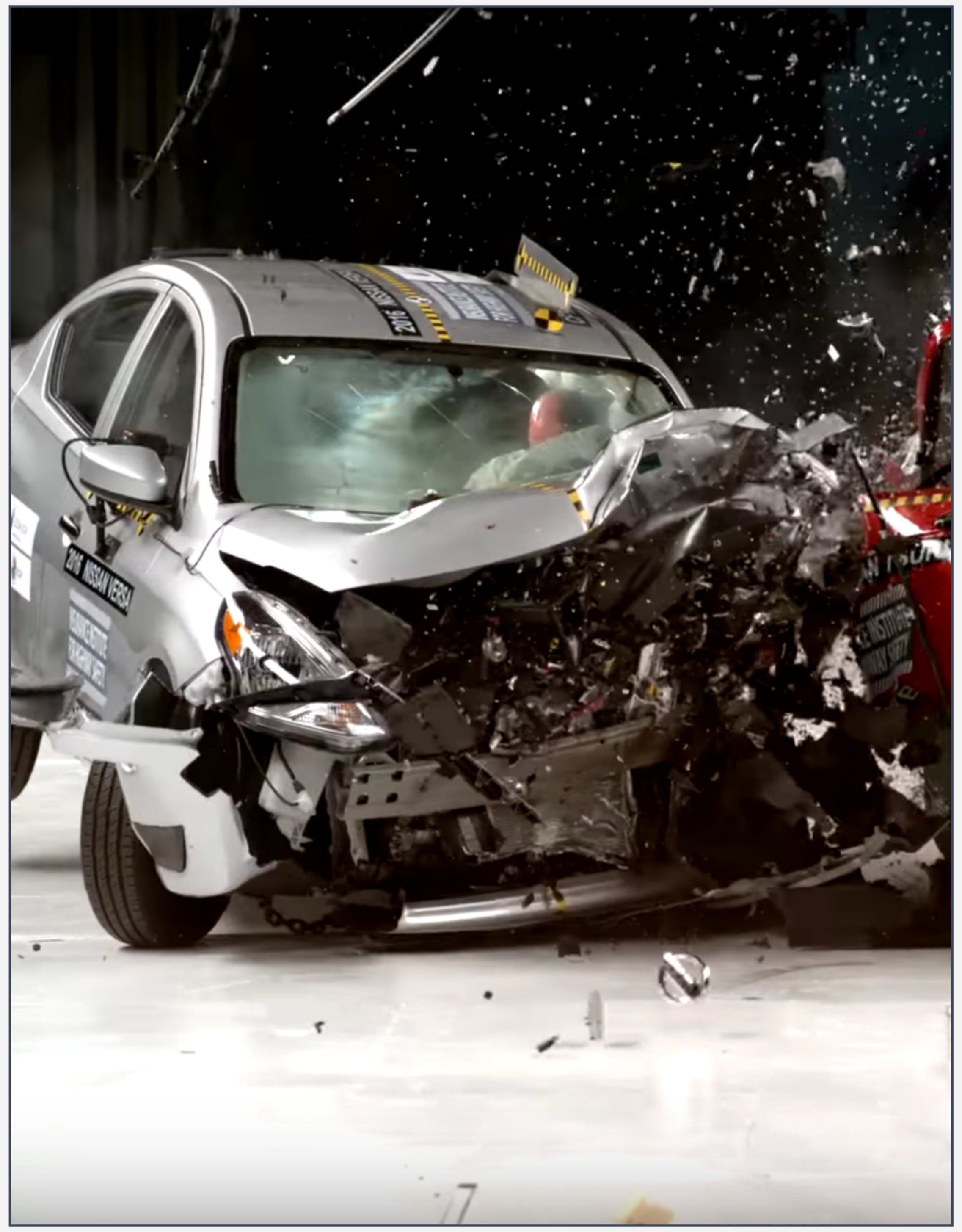
long-term properties

(creep, fatigue)



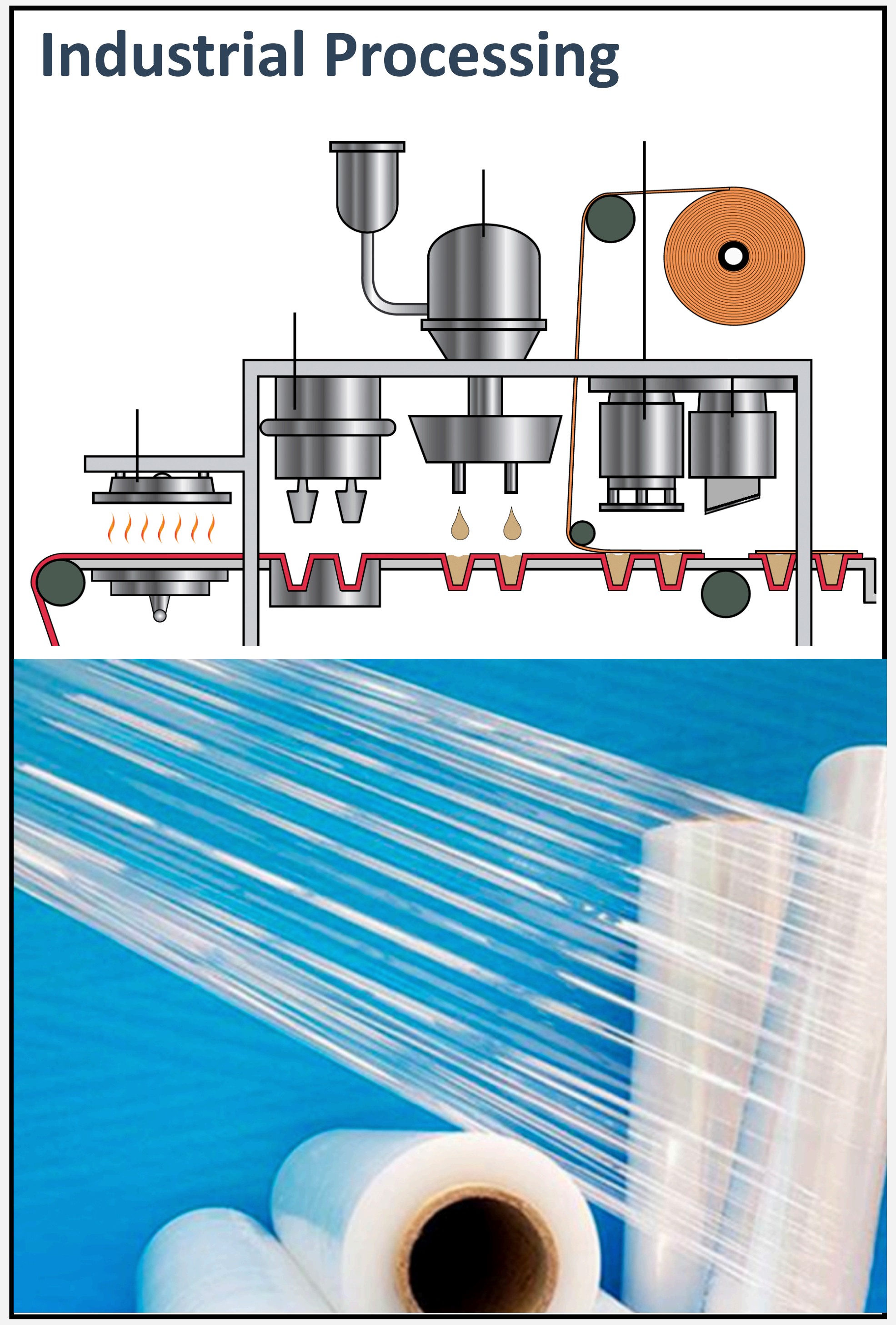
short-term properties

(impact resistance, energy dissipation, vibration,…)



processability

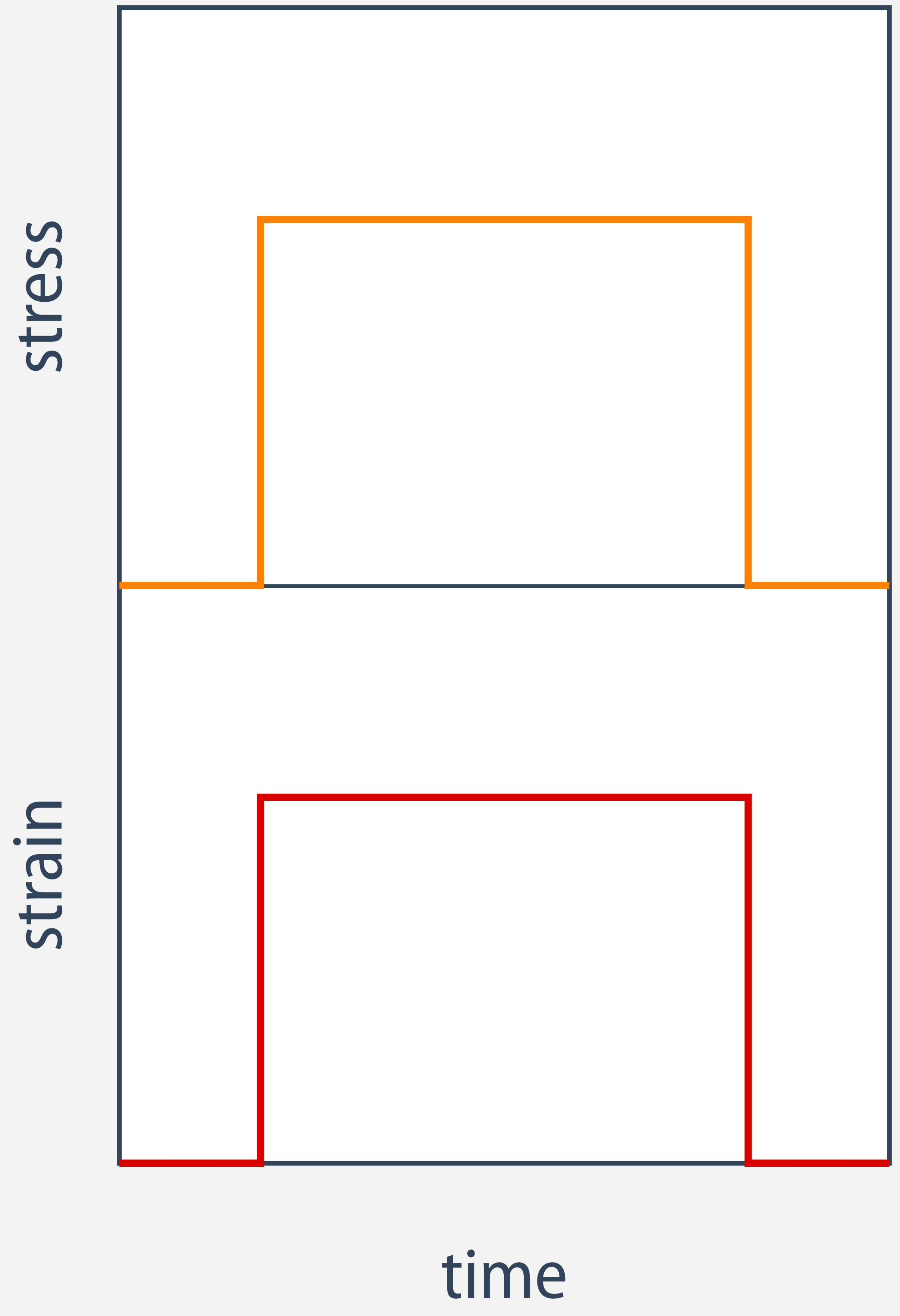
(e.g. thermoforming, fiber drawing)



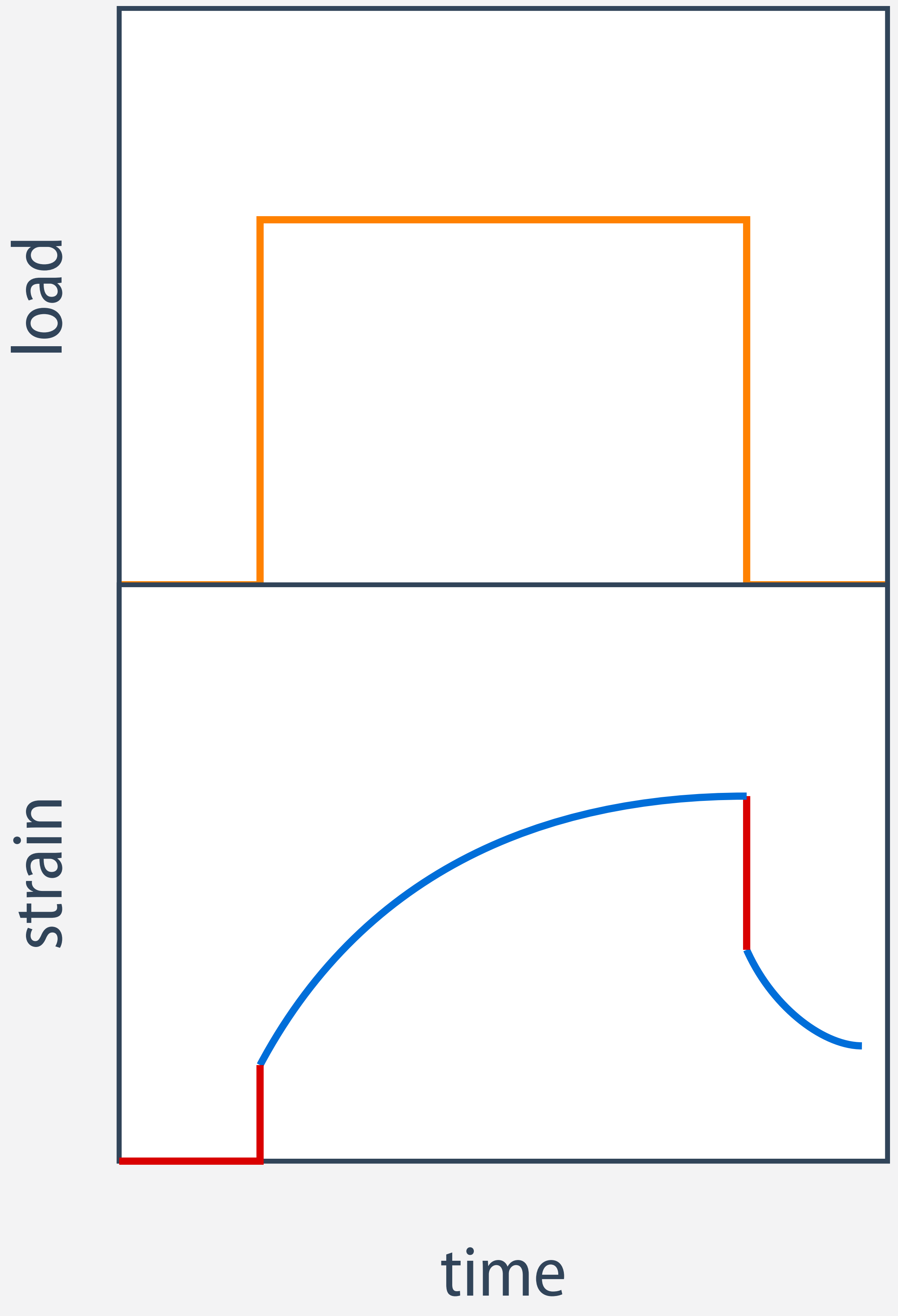
Elastic, Viscoelastic, and Viscous Responses

- step stress tests (creep experiment) illustrating the intermediate behavior of viscoelastic materials that is between perfect elasticity and perfect viscous flow:

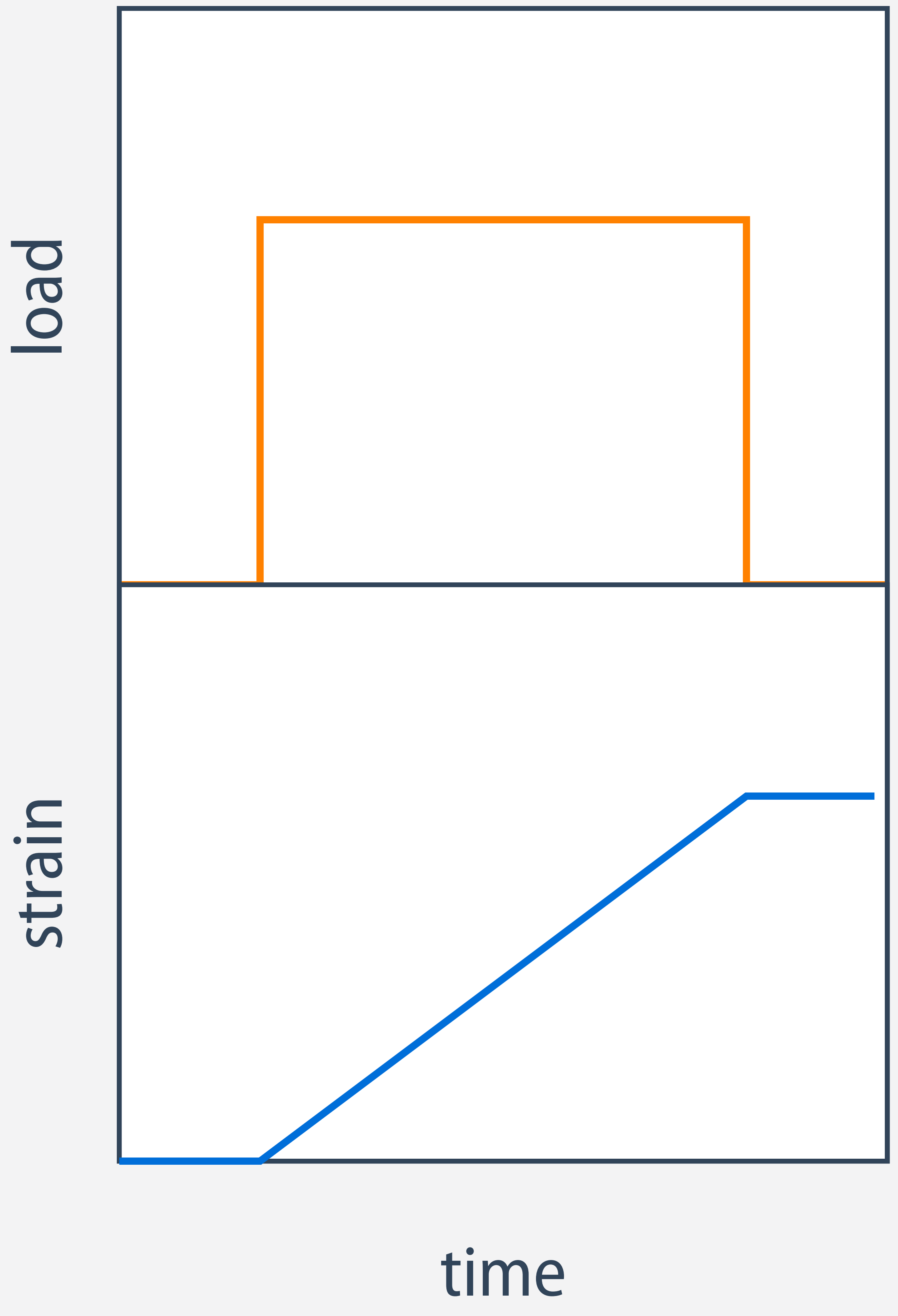
elastic solid



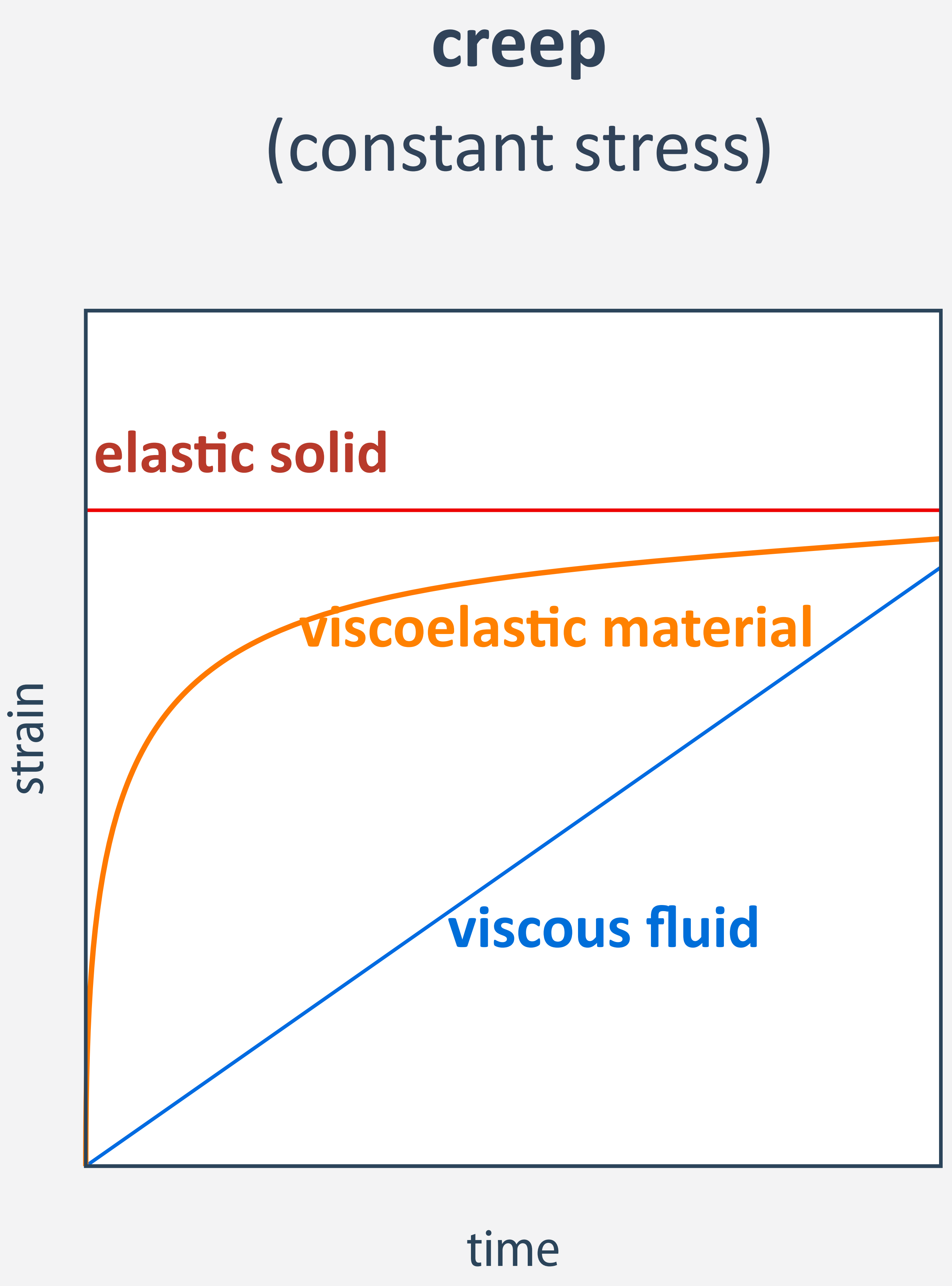
viscoelastic

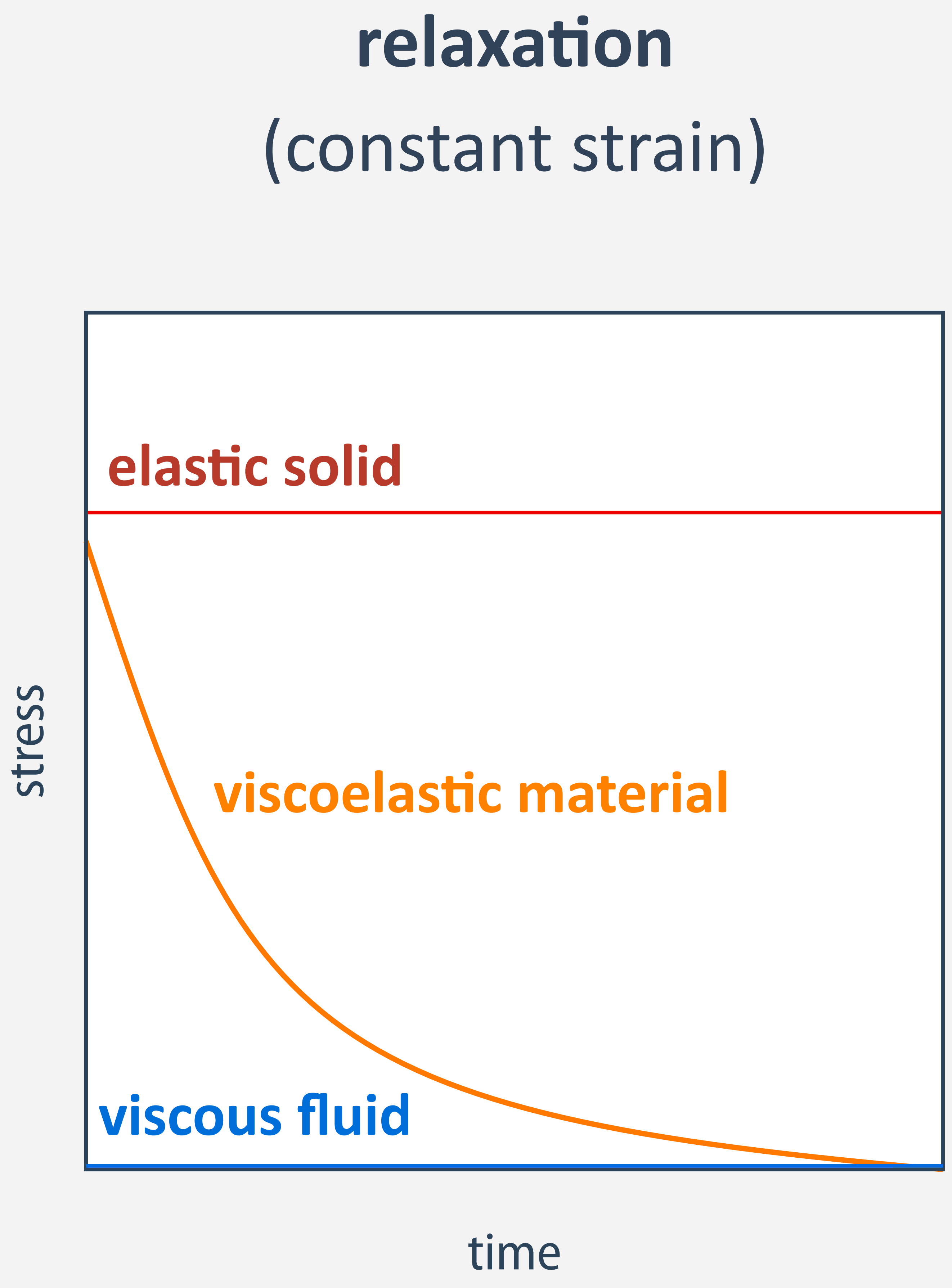


liquid flow



Phenomenological Description of Viscoelasticity



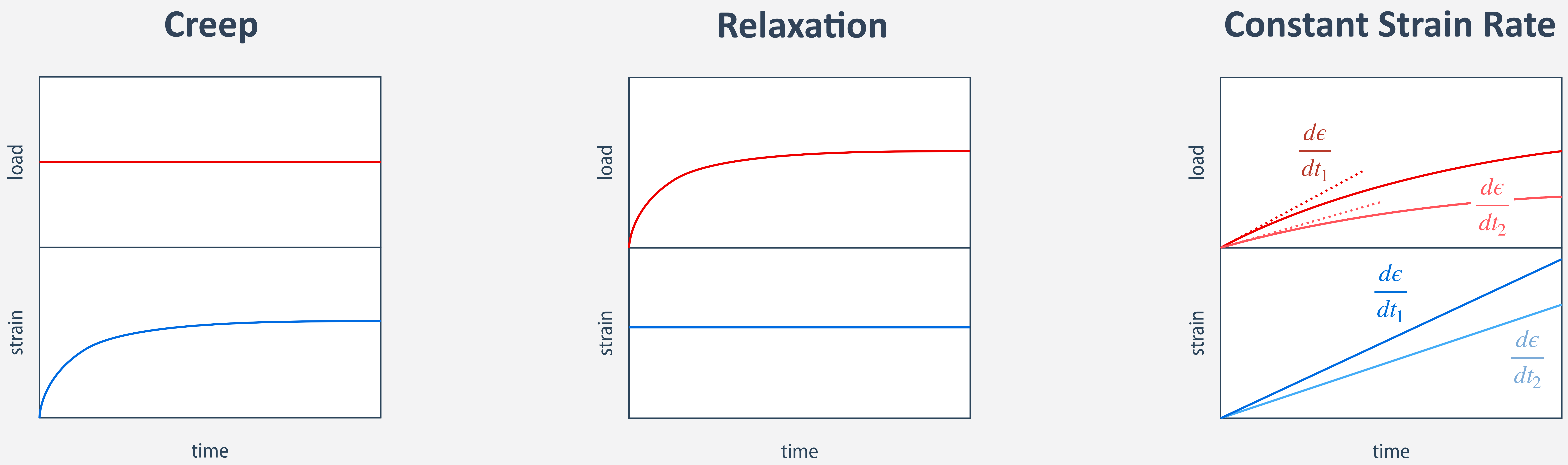


- **linear viscoelasticity: Hooke's & Newton's law can be applied, stress-independent modulus** $E = F(T, t)$ (valid for small deformations)
- **non-linear viscoelasticity in case of large deformations: stress-dependent** $E = F(T, t, \sigma)$

Linear Viscoelasticity

Influence of Time on Stress and Strain

- static creep and relaxation tests to determine the viscoelastic functions for tension and shear deformation



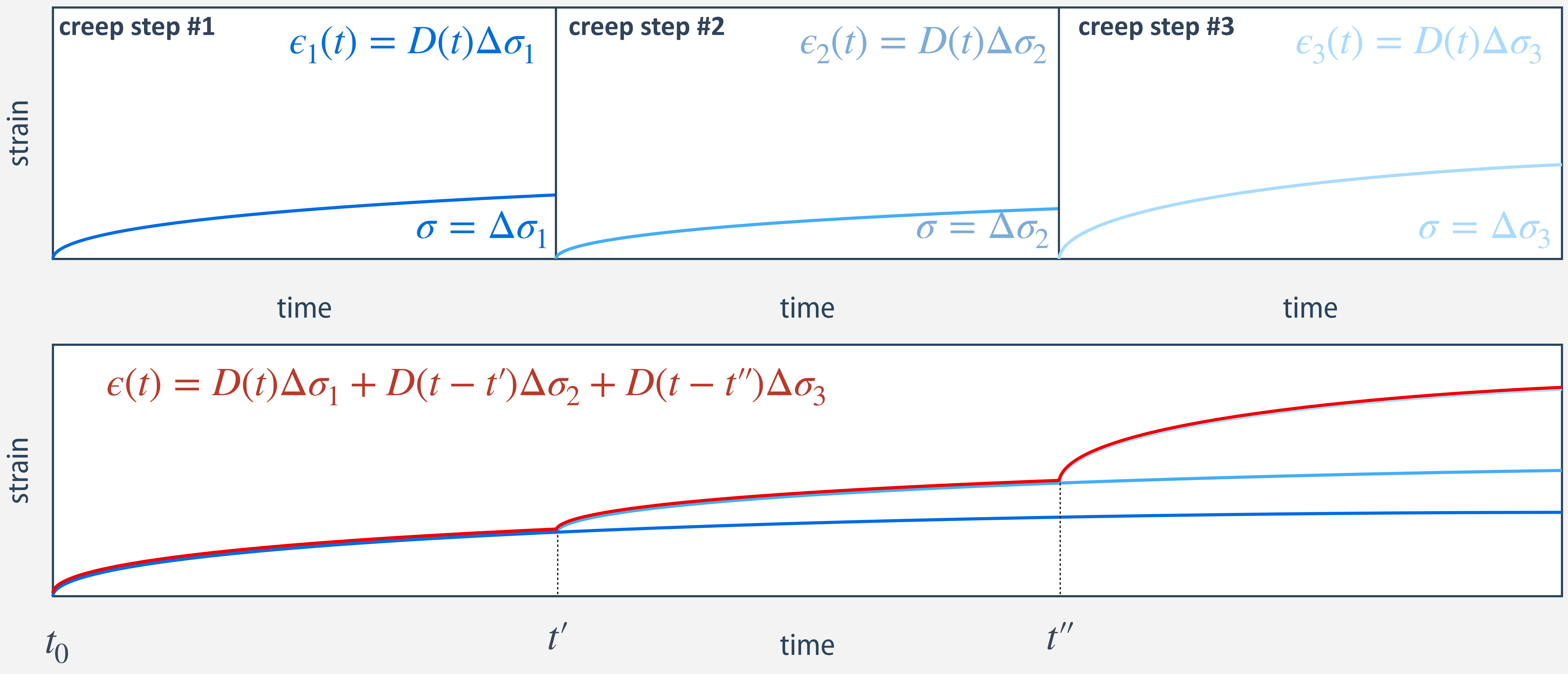
$$\mathrm{D}(t) = \frac{\epsilon(t)}{\sigma_0} \qquad \mathrm{J}(t) = \frac{\gamma(t)}{\sigma_0}$$

$$\mathrm{E}(t) = \frac{\sigma(t)}{\epsilon_0} \qquad \mathrm{G}(t) = \frac{\sigma(t)}{\gamma_0}$$

- **the viscoelastic functions $\mathrm{D}(t)$ and $\mathrm{J}(t)$ are compliances, $\mathrm{E}(t)$ and $\mathrm{G}(t)$ are moduli**
- **don't confuse with the time-independent Young's modulus!** $E = 1/D$ (only for Hookean solids)

Boltzmann's Superposition Principle

- state of stress or strain is a function of the history of all stresses applied to the material

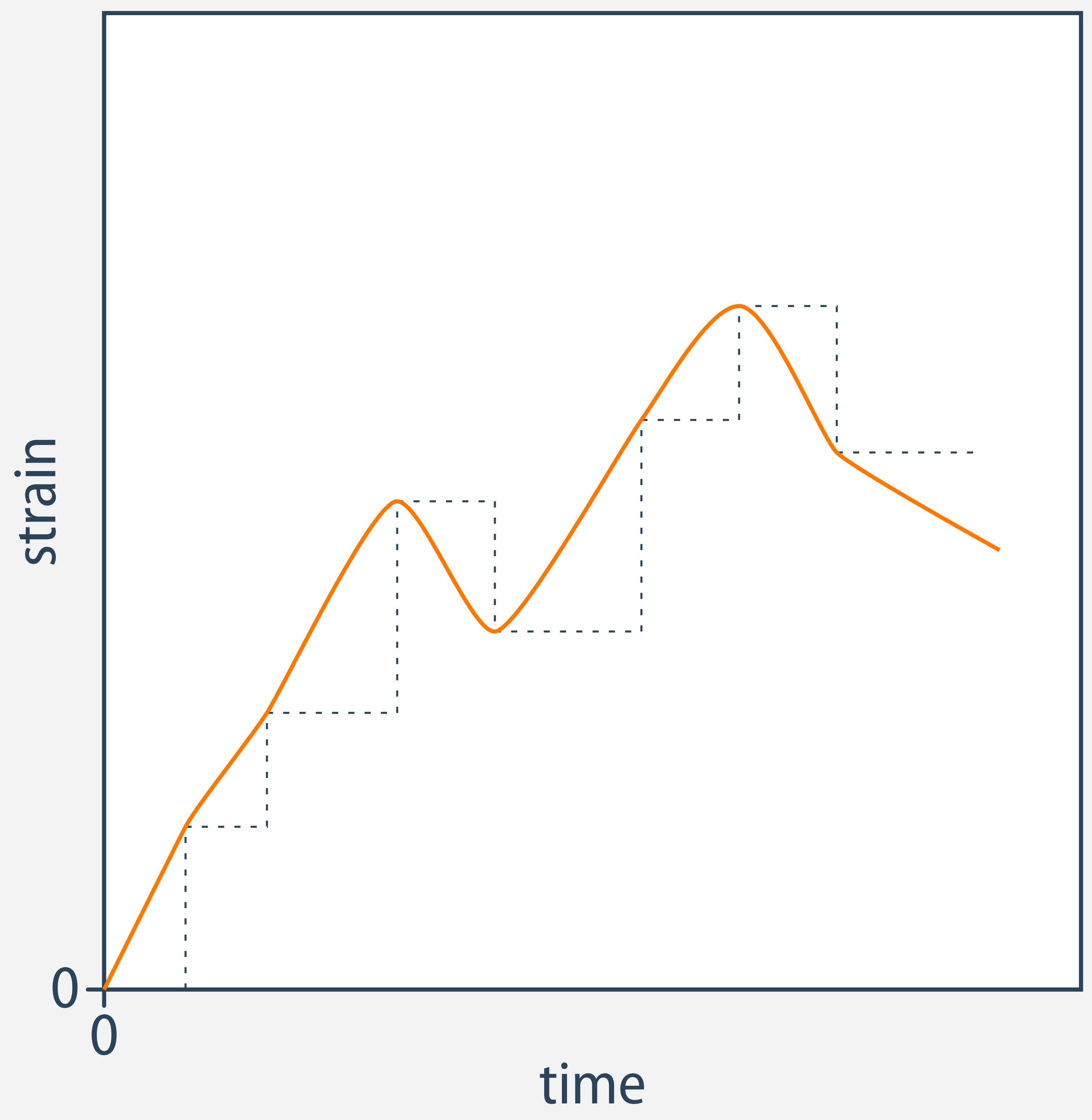


- generalized: $\epsilon(t) = \sum_{n=0} D(t - t_n)\Delta\sigma_n$
- the material keeps a "memory" of all its stresses (or deformations).

Boltzmann's Superposition Principle in the Continuous Limit

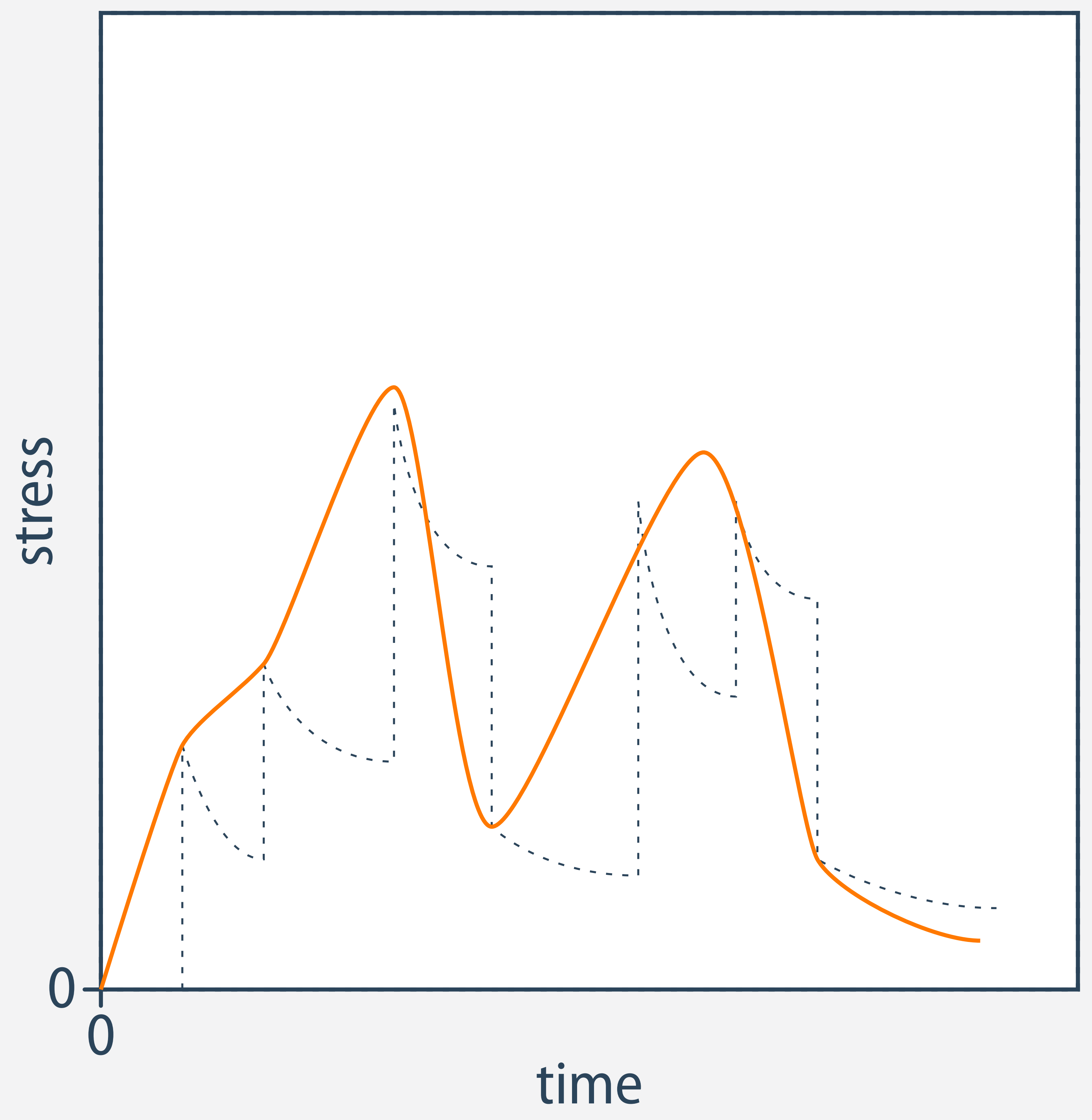
- for an infinite number of strain increments: Boltzmann superposition integral

creep experiment:



$$\epsilon(t) = \int_{-\infty}^{t} D(t-t')\frac{d\sigma}{dt'}dt'$$

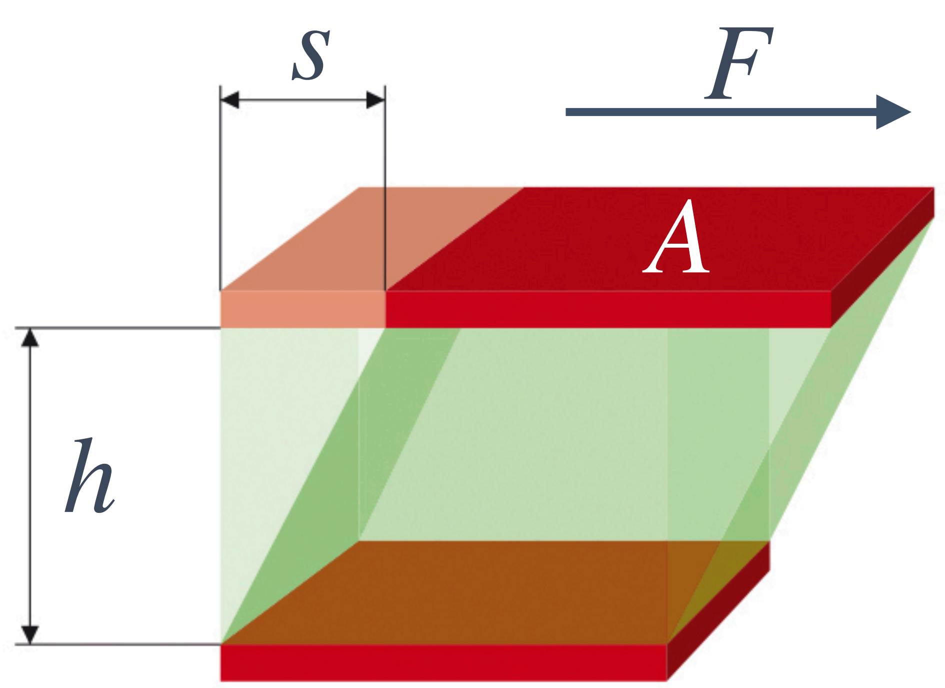
for stress relaxation



$$\sigma(t) = \int_{-\infty}^{t} E(t-t')\frac{d\epsilon}{dt'}dt'$$

Dynamic Mechanical Analysis

- **small strain experiments are conveniently carried out under shear.**



shear stress: $\sigma = \dfrac{F}{A}$

shear strain: $\gamma = \dfrac{s}{h}$

shear modulus: $G = \dfrac{\sigma}{\gamma}$

material	shear modulus (G)
very soft gel structures (salad dressing)	5-10 Pa
soft gel structures (coatings, paints)	10-50 Pa
viscoelastic gels (dispersions, lotions,…)	50-5’000 Pa
gummy bears	10-500 kPa
car tires (hard rubbers)	10-100 MPa
thermoplastic polymers	0.1-2 GPa
ceramics, glass	15 - 35 GPa
aluminum	28 GPa
steel	80 GPa

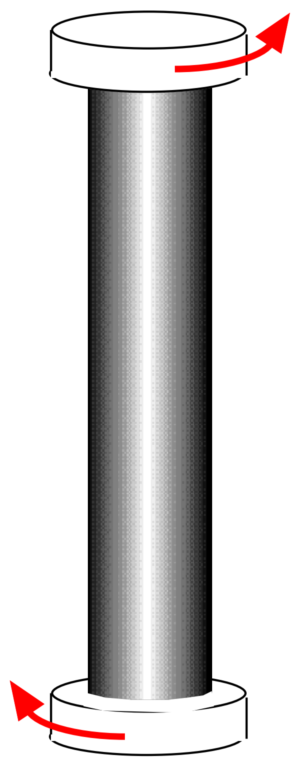
- **the higher G, the stiffer the material**

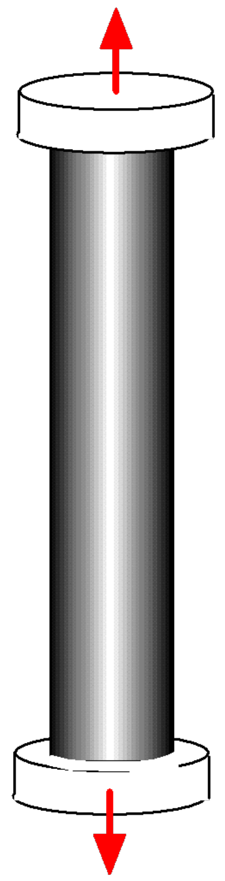
Dynamic Mechanical Measurements

- **samples subjected to dynamic or oscillatory stress (or deformation), commonly under shear**
  (but also in tension and bending possible)

dynamic mechanical analysis (DMA)

shear or tensile deformation



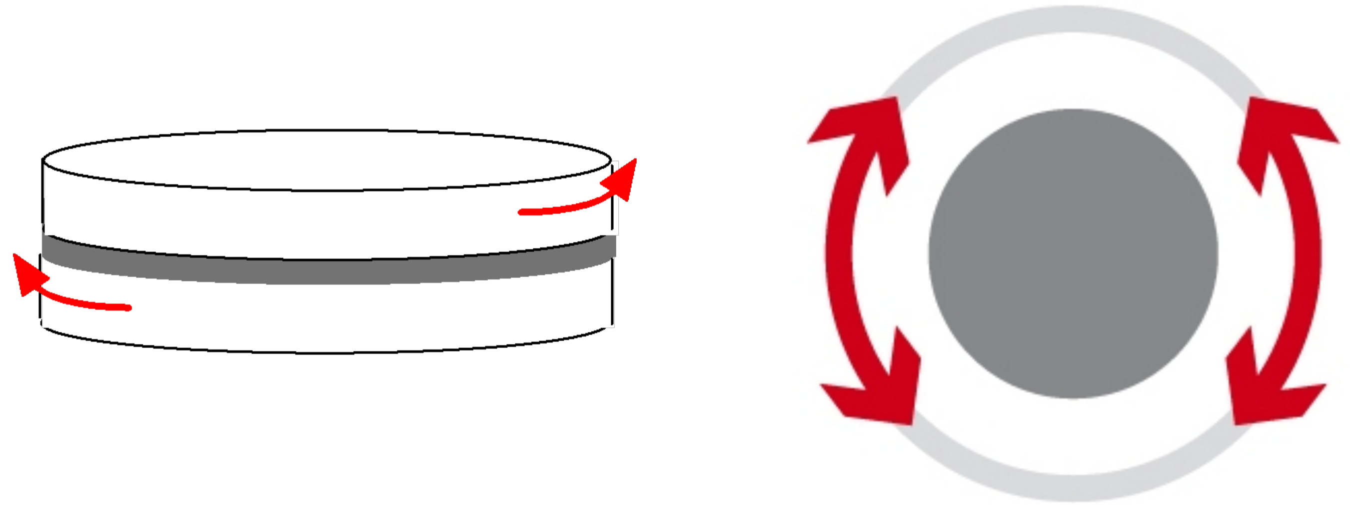


$\gamma(t) = \gamma_0 sin(\omega t)$ $\epsilon(t) = \epsilon_0 sin(\omega t)$

typical for solid samples

rheometry

usually shear deformation



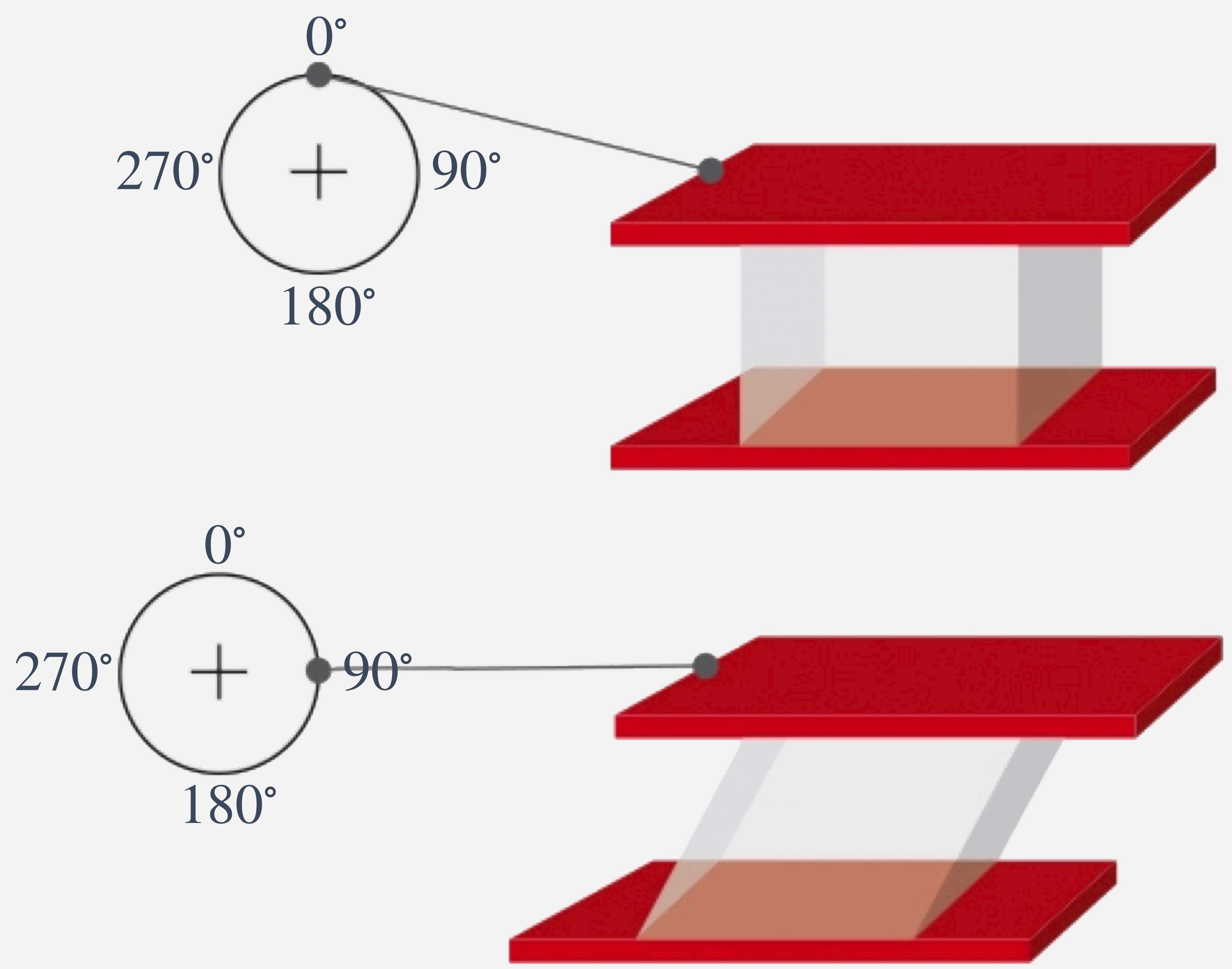
$\gamma(t) = \gamma_0 sin(\omega t)$

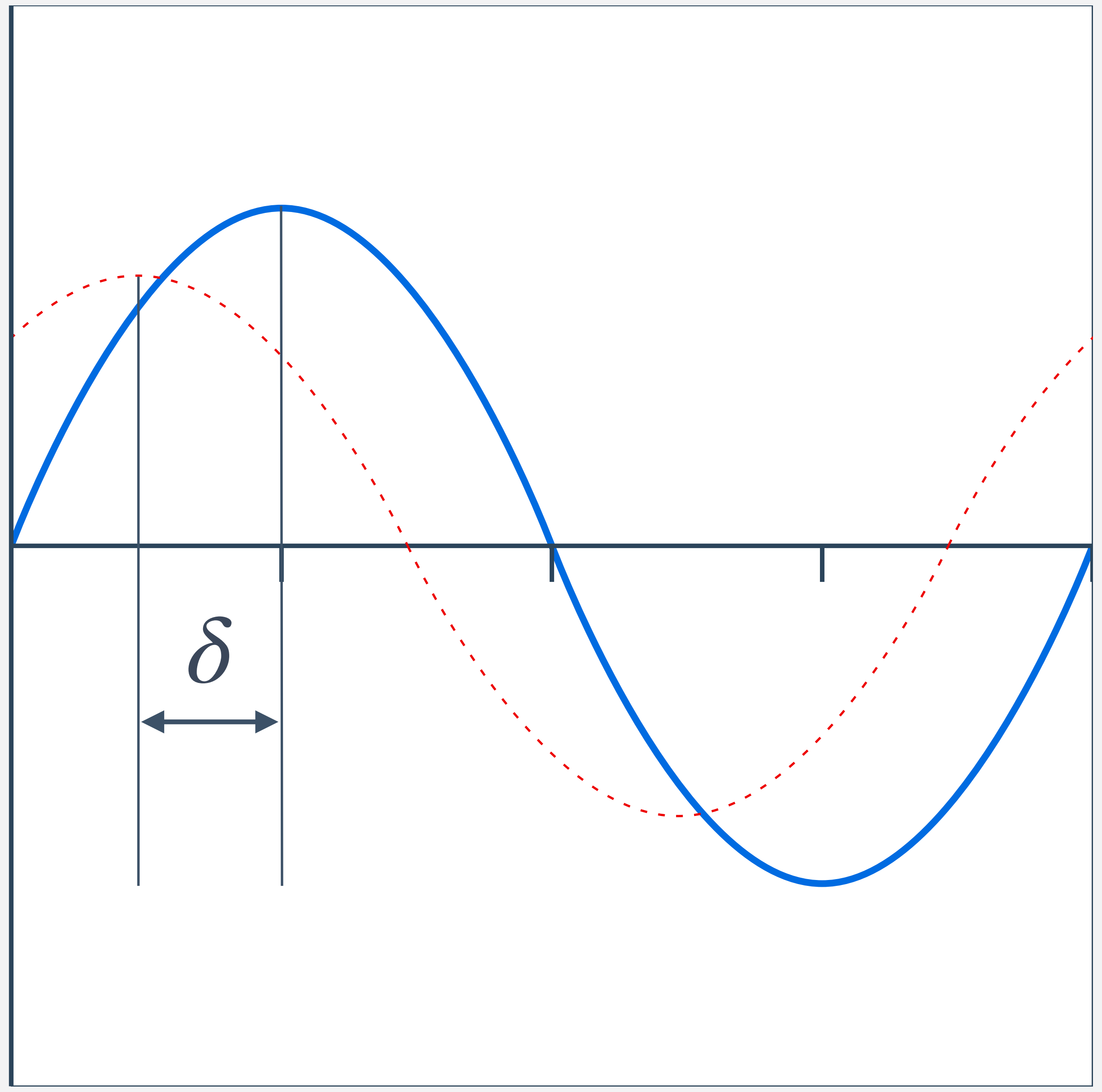
typical for liquids

- **stresses measured as function of T (constant ω) or as function of ω (constant T)**

Periodic Deformation

- materials can be examined in their solid and liquid state by oscillatory tests





$\sigma(t) = G\gamma = \sigma_0 sin(\omega t + \delta)$

$\gamma(t) = \gamma_0 sin(\omega t)$

Hookean solid

$\delta = 0°$

viscoelastic material

$0° < |\delta| < 90°$

Newtonian fluid

$\delta = 90°$

- parameters for oscillatory tests are usually preset in the form of a sine curve

Storage Modulus, Loss Modulus & Loss Factor

$$\gamma(t) = \gamma_0 sin(\omega t)$$

$$\sigma(t) = \sigma_0 sin(\omega t + \delta) = \sigma_0(sin(\omega t)cos(\delta) + cos(\omega t)sin(\delta))$$

$$\frac{\sigma(t)}{\gamma_0} = \frac{\sigma_0}{\gamma_0}(sin(\omega t)cos(\delta)) + \frac{\sigma_0}{\gamma_0}(cos(\omega t)sin(\delta)) \quad \equiv G' sin(\omega t) + G'' cos(\omega t)$$

storage modulus:

$$G' = \frac{\sigma_0}{\gamma_0}cos(\delta)$$

loss modulus:

$$G'' = \frac{\sigma_0}{\gamma_0}sin(\delta)$$

loss factor:

$$tan(\delta) = \frac{G''}{G'}$$

- **storage modules G': elastic portion of the viscoelastic behavior** (stored deformation energy)
- **loss modulus G'': viscous portion of the viscoelastic behavior** (dissipated energy during viscous flow)
- **loss factor or damping factor $tan(\delta)$: ratio between G'' and G'** (maxima often indicate phase transitions)

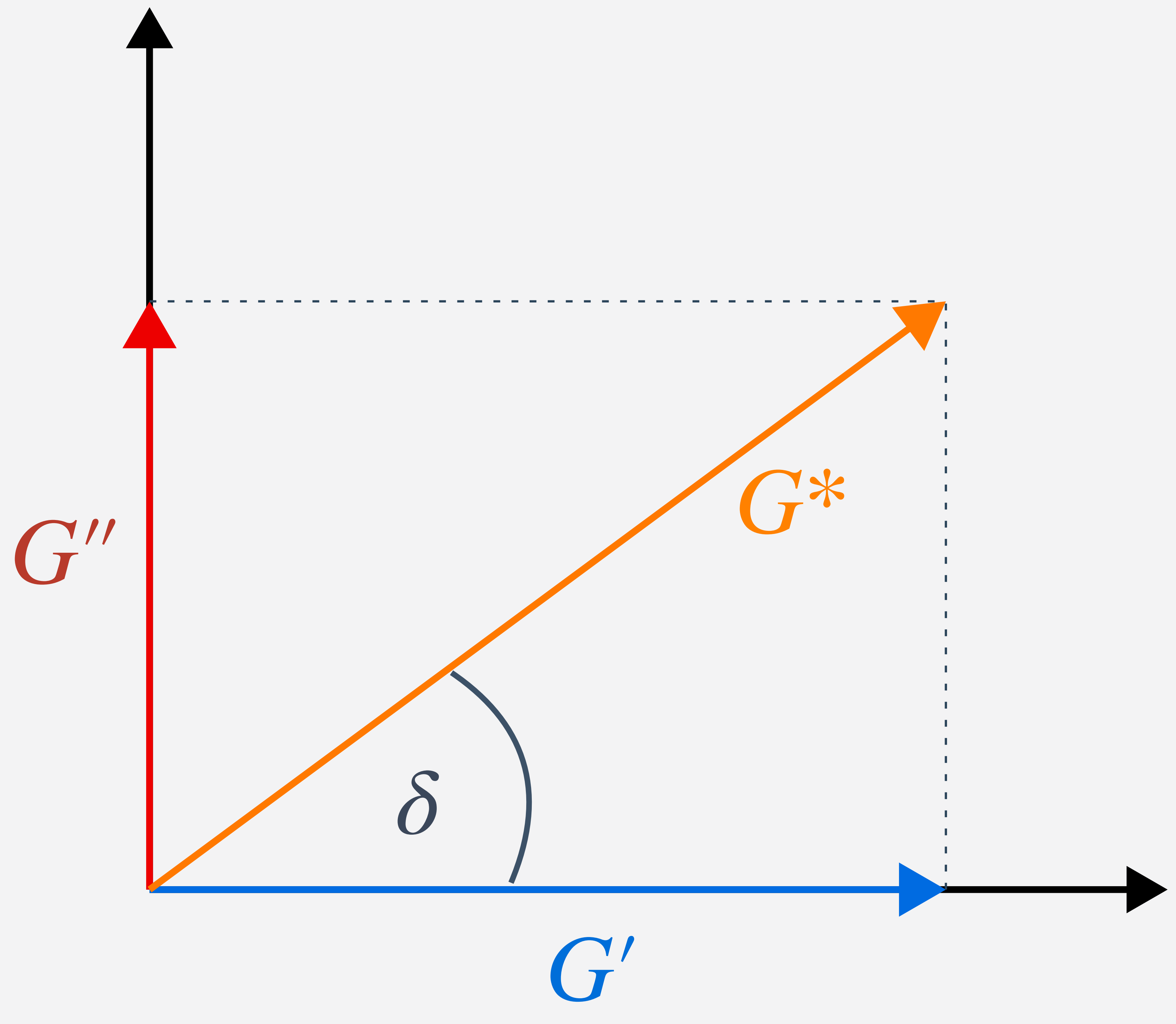
Complex Moduli

- **the entire viscoelastic behavior is described by the complex shear modulus $G*$**

$$G* = \frac{\sigma*}{\gamma*} = \frac{\sigma_0 e^{i(\omega t+\delta)}}{\gamma_0 e^{(i\omega t)}}$$

$$= \frac{\sigma_0 e^{(i\delta)}}{\gamma_0} = \frac{\sigma_0(cos(\delta) + i\ sin(\delta))}{\gamma_0}$$

$$= G' + iG''$$



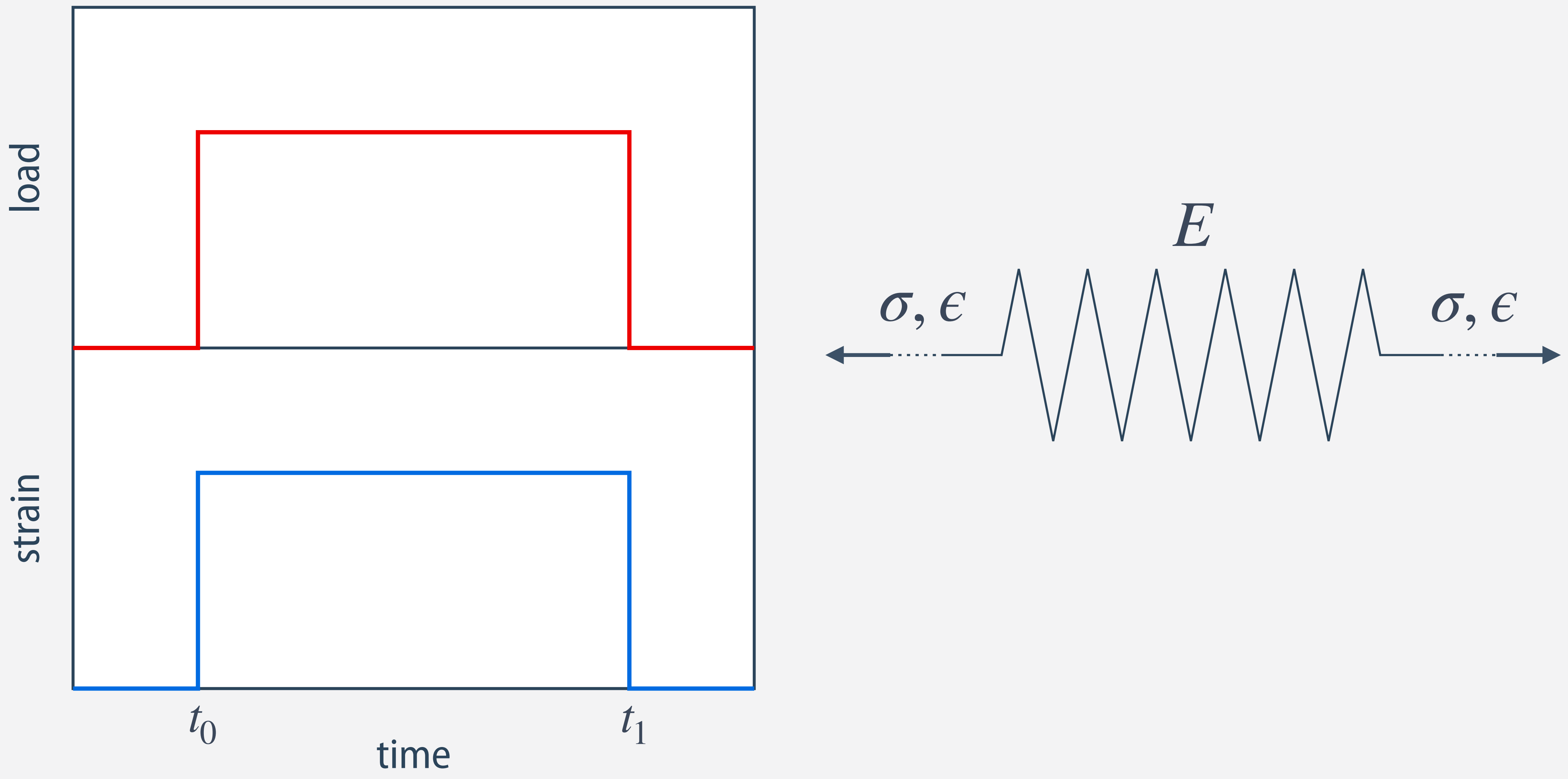
viscoelastic solids: $G' > G''$

viscoelastic liquids: $G'' > G'$

- **the storage and loss moduli are called the real and imaginary parts of the complex modulus**

Simple Mechanical Models

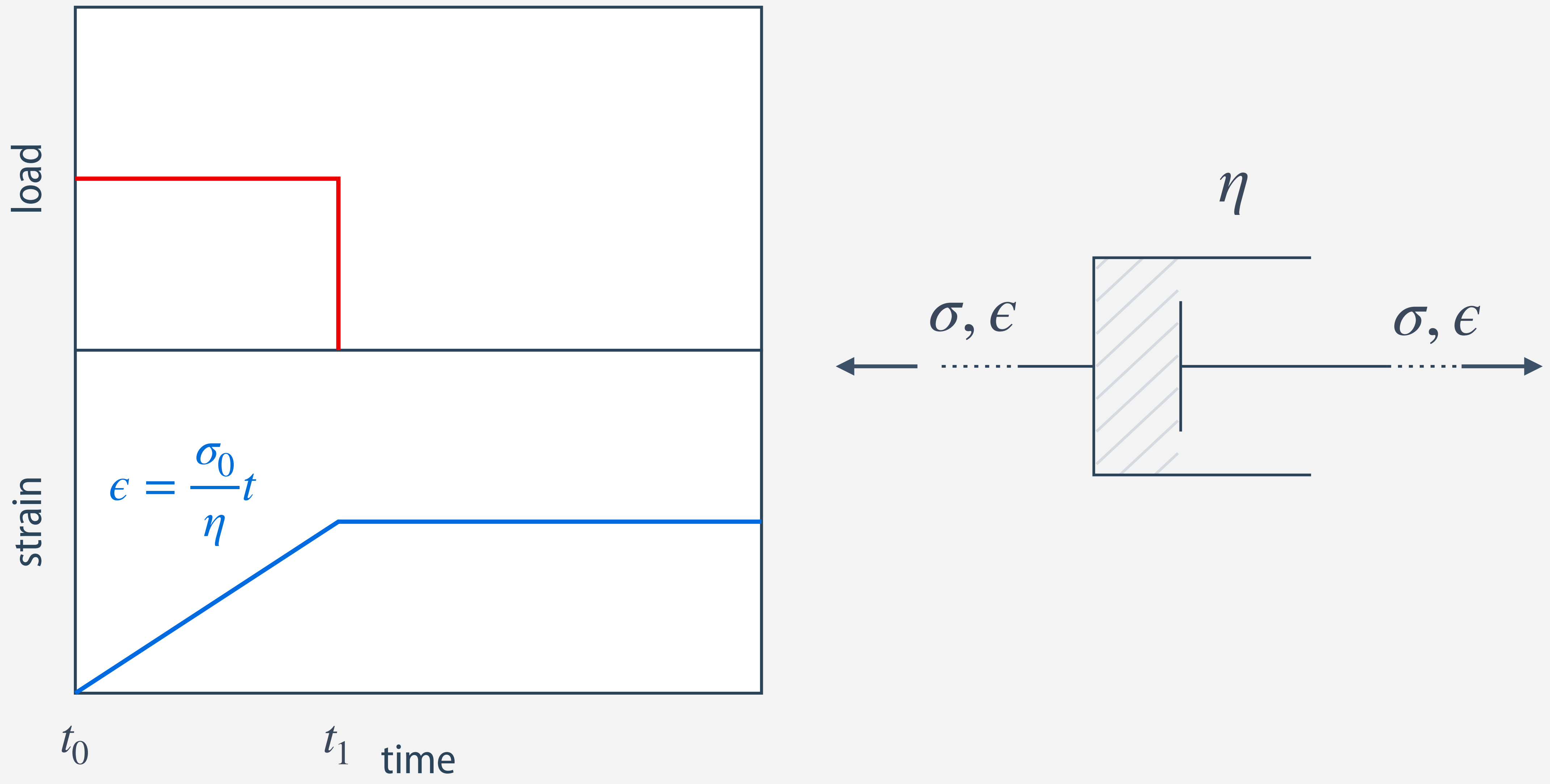
elastic solids
reversible deformation



Hooke's law:

$$\sigma = E\epsilon$$

viscous liquids
irreversible deformation



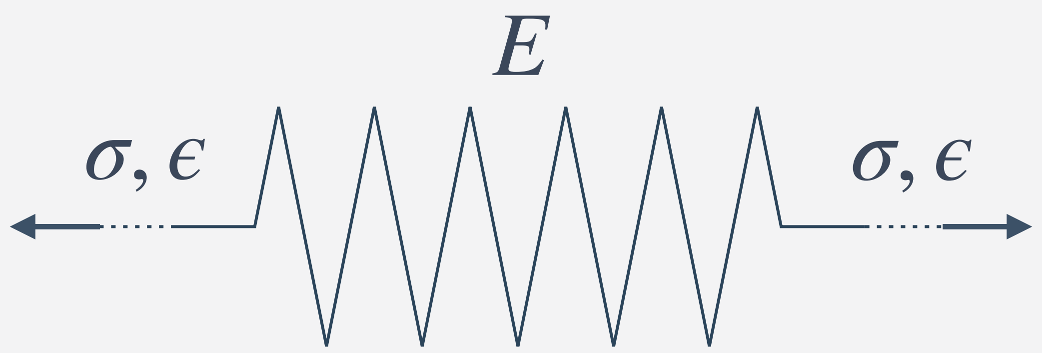
Newton's law:

$$\dot{\epsilon} = \frac{\sigma}{\eta}$$

- **simple mechanical models to describe elasticity (spring) or viscous flow (dashpot)**

Simple Viscoelastic Models: Linear Combinations of Dashpots & Elastic Springs

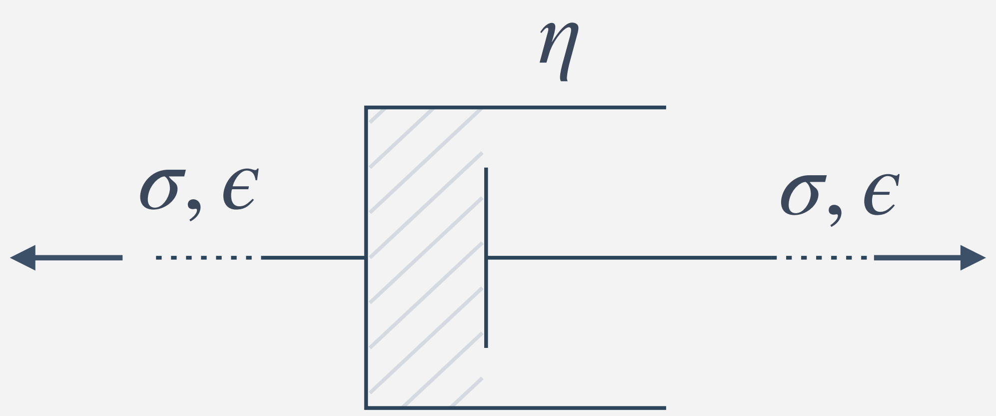
elastic solids



Hooke's law:

$$\sigma = E\epsilon$$

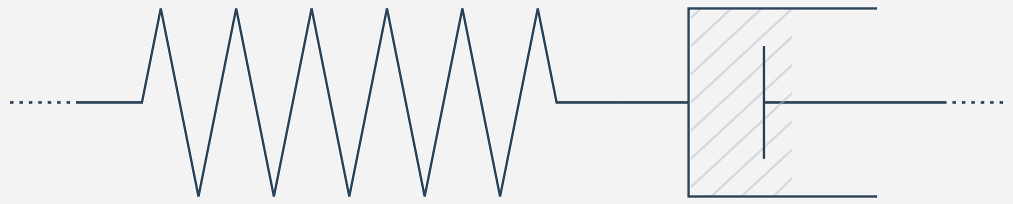
viscous liquids



Newton's law:

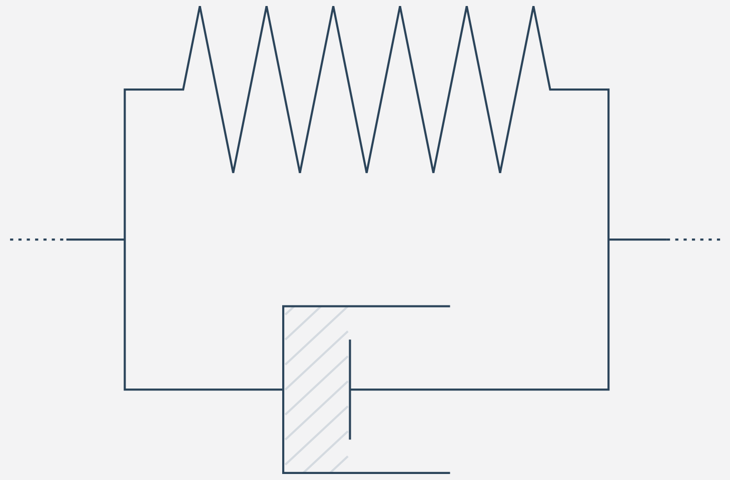
$$\dot{\epsilon} = \frac{\sigma}{\eta}$$

Maxwell model



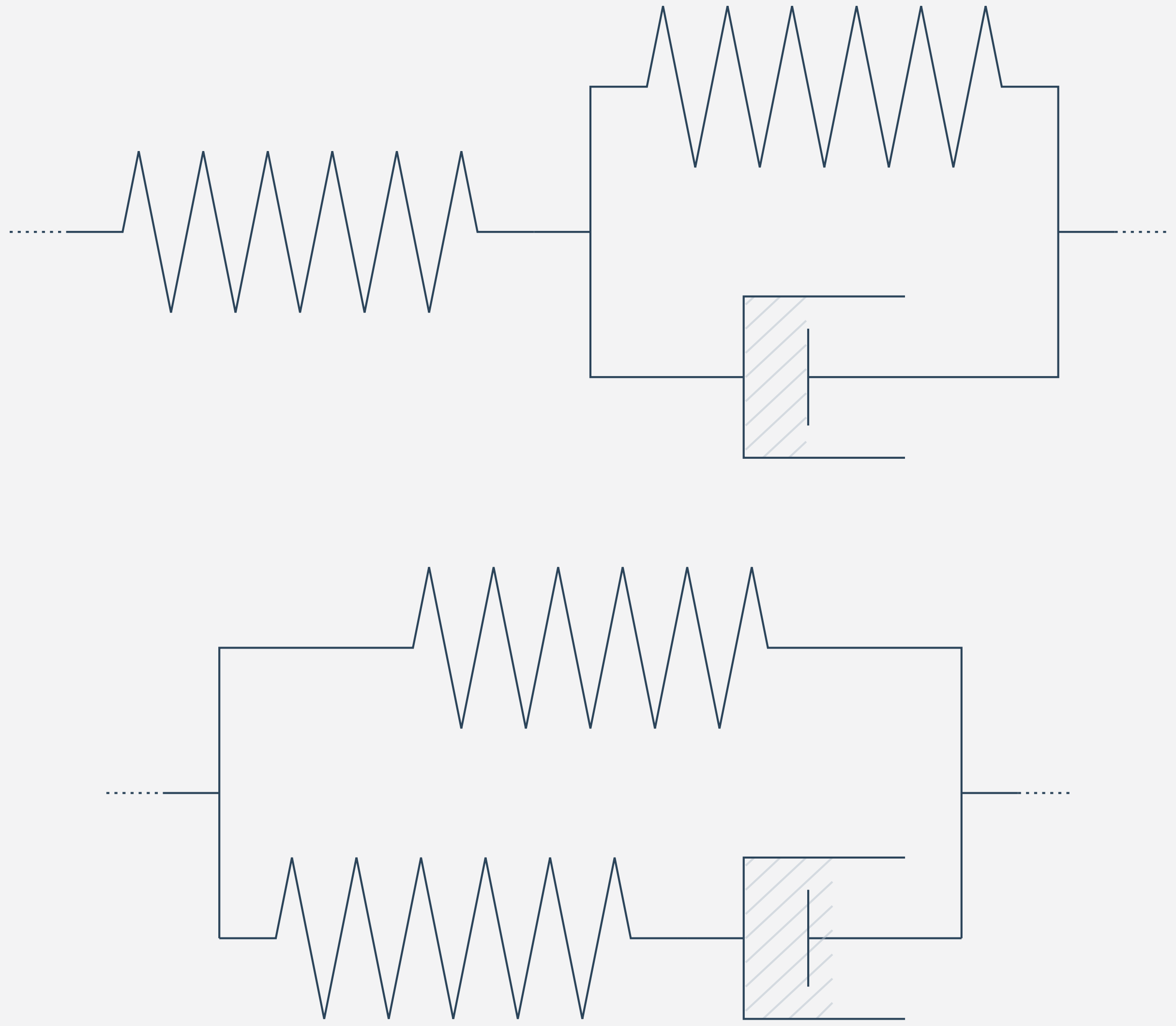
$$\sigma = \sigma_1 = \sigma_2$$
$$\epsilon = \epsilon_1 + \epsilon_2$$

Voigt model



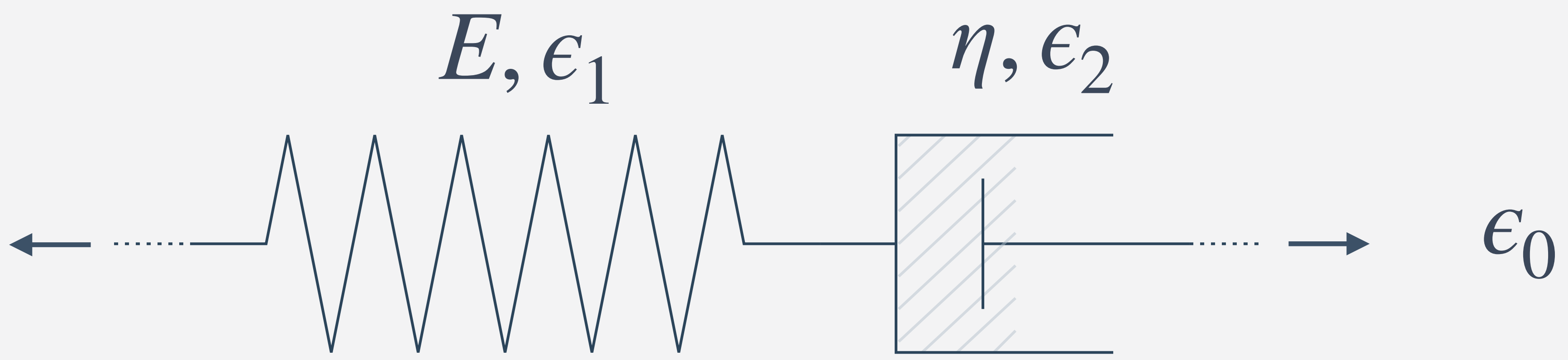
$$\sigma = \sigma_1 + \sigma_2$$
$$\epsilon = \epsilon_1 = \epsilon_2$$

Zener models (standard linear solid)



Maxwell Model

- **for a relaxation experiment using an elastic spring and dashpot combined in series:**



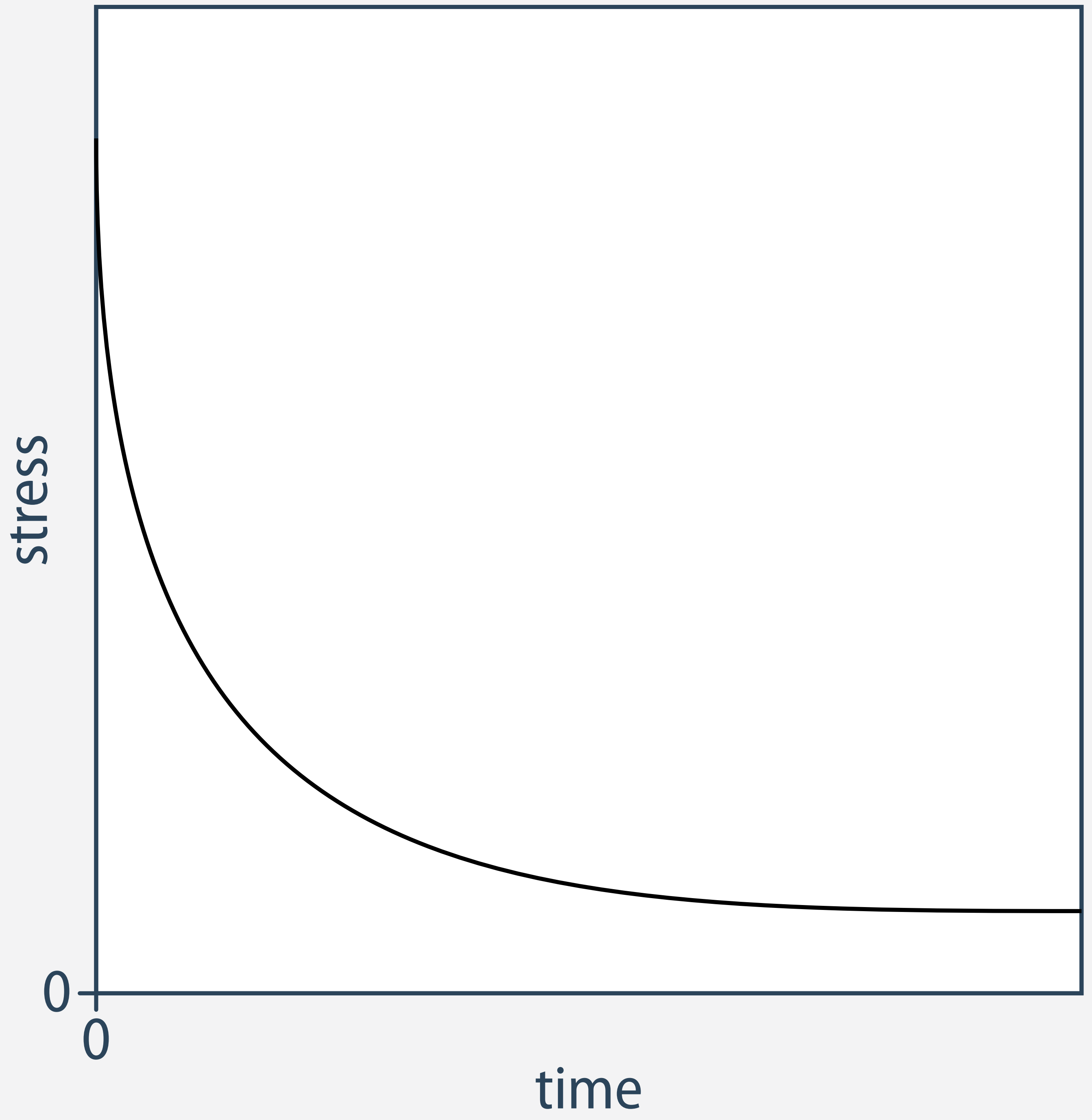
$\epsilon = \epsilon_1 + \epsilon_2 = \epsilon_0 =$ constant
(for a relaxation experiment)

$$\frac{d\epsilon}{dt} = \frac{d\epsilon_1}{dt} + \frac{d\epsilon_2}{dt} = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta} = 0$$

$$\frac{d\sigma}{\sigma} = -\frac{E}{\eta}dt \quad \rightarrow \quad [ln(\sigma)]_{\sigma_0}^{\sigma} = -\frac{E}{\eta}[t']_0^t$$

$$\sigma = \sigma_0 e^{(-t/\tau)} \quad \text{with} \quad \tau = \frac{\eta}{E}$$

$$\mathrm{E}(t) = \frac{\sigma}{\epsilon_0} = \frac{\sigma_0}{\epsilon_0}e^{(-t/\tau)} = Ee^{(-t/\tau)}$$



- **reasonable qualitative description of stress relaxation by the relaxation time τ**

Maxwell Behavior under Dynamic Deformation

- **relaxation dynamics under sinusoidal deformation:** $\epsilon * = \epsilon_0 e^{(i\omega t)}$ $\quad \frac{d\epsilon *}{dt} = i\omega\epsilon_0 e^{(i\omega t)}$

- **for the stress under continuous deformation follows:**

$$\sigma * = \int_{-\infty}^{t} \mathrm{E}(t-t')\frac{d\epsilon *}{dt'}dt' = \int_{-\infty}^{t} Ee^{-\frac{t-t'}{\tau}}\epsilon_0 i\omega e^{(i\omega t')}dt'$$

see **Slide 238** and **239**

$$= \frac{Ei\omega\epsilon_0}{\frac{1}{\tau}+i\omega}\left[e^{(-\frac{t-t'}{\tau}+i\omega t')}\right]_{-\infty}^{t} = \frac{Ei\omega\epsilon_0}{\frac{1}{\tau}+i\omega}e^{i\omega t} = \frac{Ei\omega\epsilon_0(\frac{1}{\tau}-i\omega)}{\frac{1}{\tau^2}+\omega^2}e^{i\omega t} = \frac{Ei\epsilon_0(\omega\tau-i(\omega\tau)^2)}{1+(\omega\tau)^2}e^{i\omega t}$$

- **the complex modulus and loss factor are then given by:**

$$E* = \frac{\sigma *}{\epsilon *} = \frac{Ei(\omega\tau-i(\omega\tau)^2)}{1+(\omega\tau)^2} = \frac{E(\omega\tau)^2}{1+(\omega\tau)^2} + \frac{iE\omega\tau}{1+(\omega\tau)^2} = E' + iE''$$

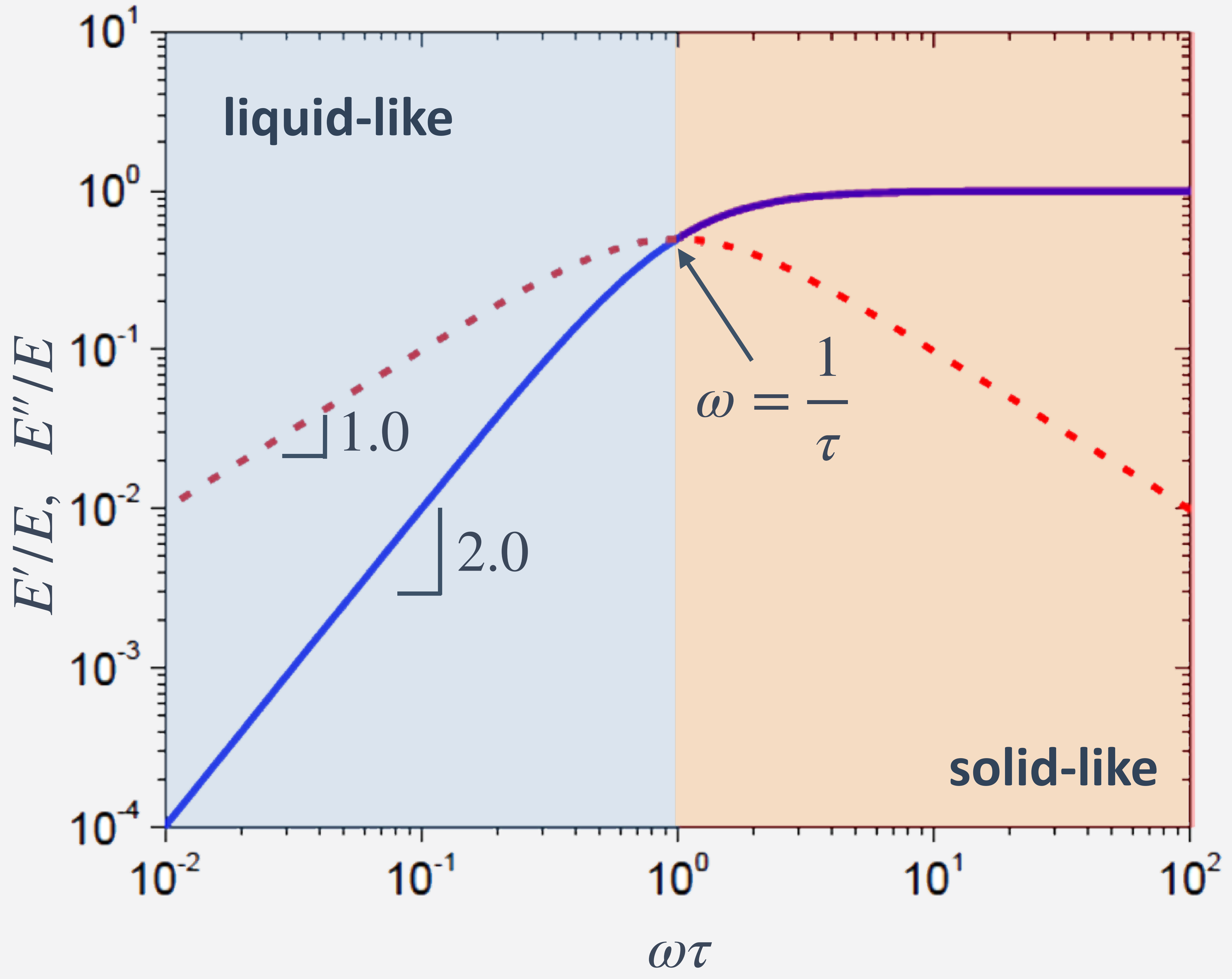
$$tan(\delta) = \frac{E''}{E'} = \frac{1}{\omega\tau}$$

Modelling Rheology Curves

- for the complex modulus it follows:

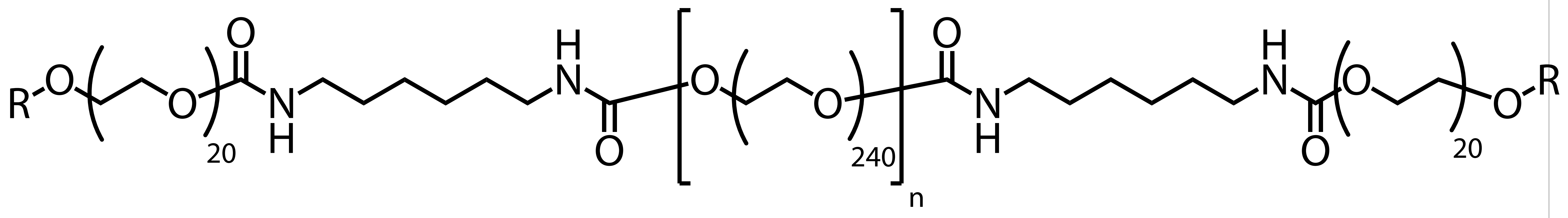
$$= E^* = \frac{\sigma^*}{\epsilon^*} = \frac{Ei\omega}{\frac{1}{\tau} + i\omega}$$

$$= E' + iE'' = \frac{E(\omega\tau)^2}{1 + (\omega\tau)^2} + \frac{iE\omega\tau}{1 + (\omega\tau)^2}$$



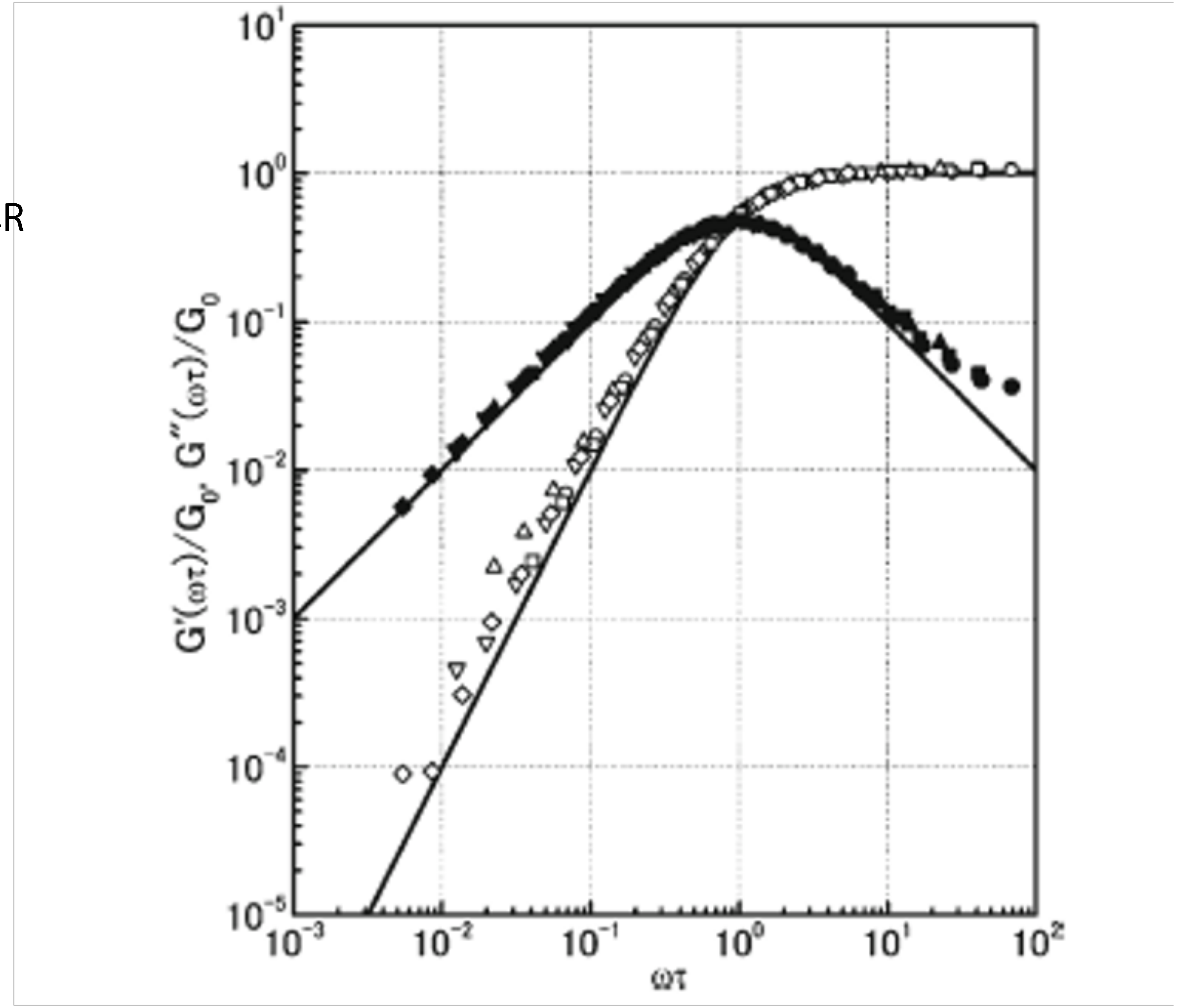
- the relaxation time characterizes the transition from liquid-like to solid-like behavior.
- universal proportionality of E' and E'' to the frequency in the terminal regime $(\omega \ll \tau)$

- **Maxwell behavior is often encountered in temporary networks from small molecules (due to the formation of hydrogen-bonds, for example) with a single relaxation time.**

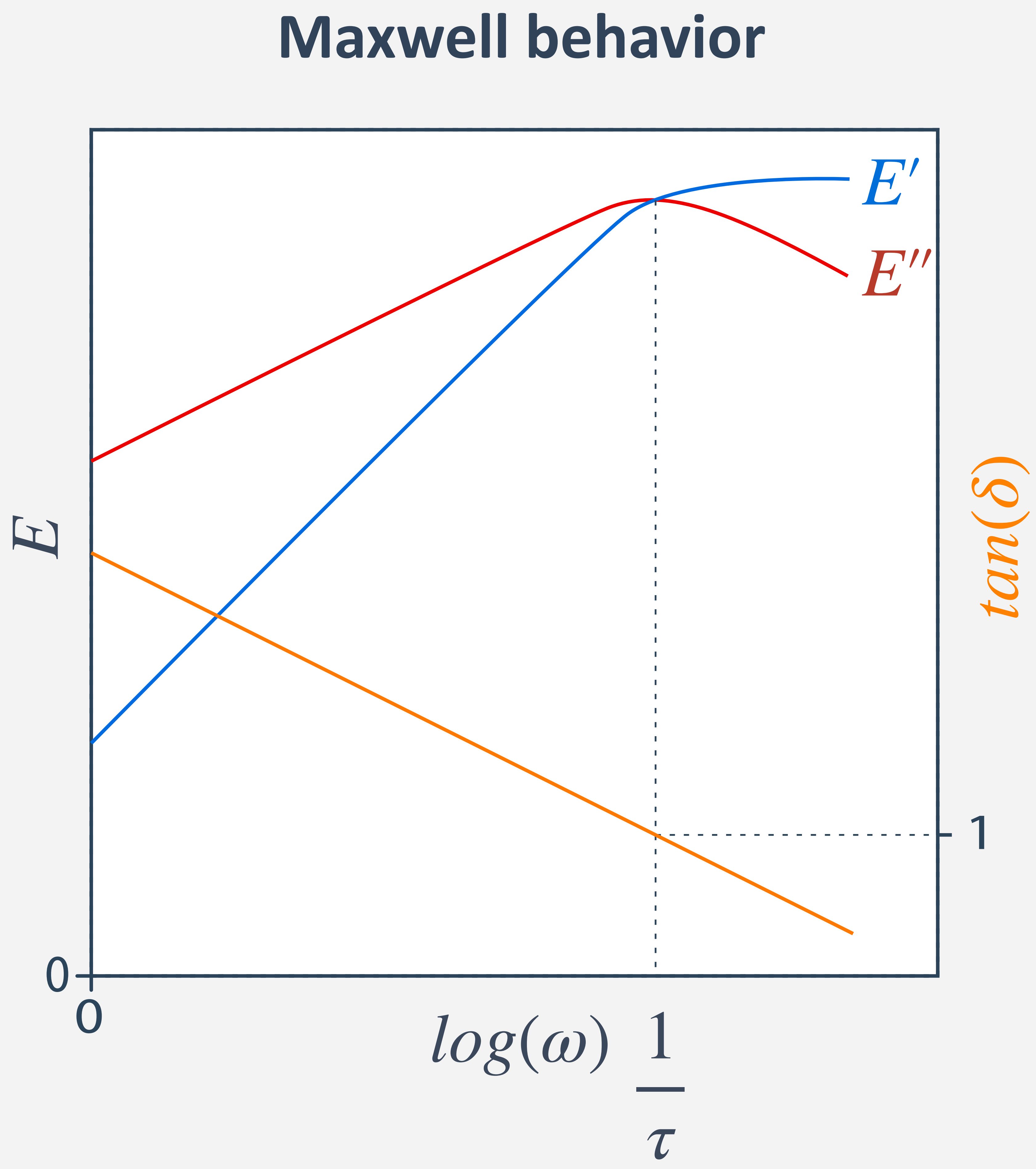


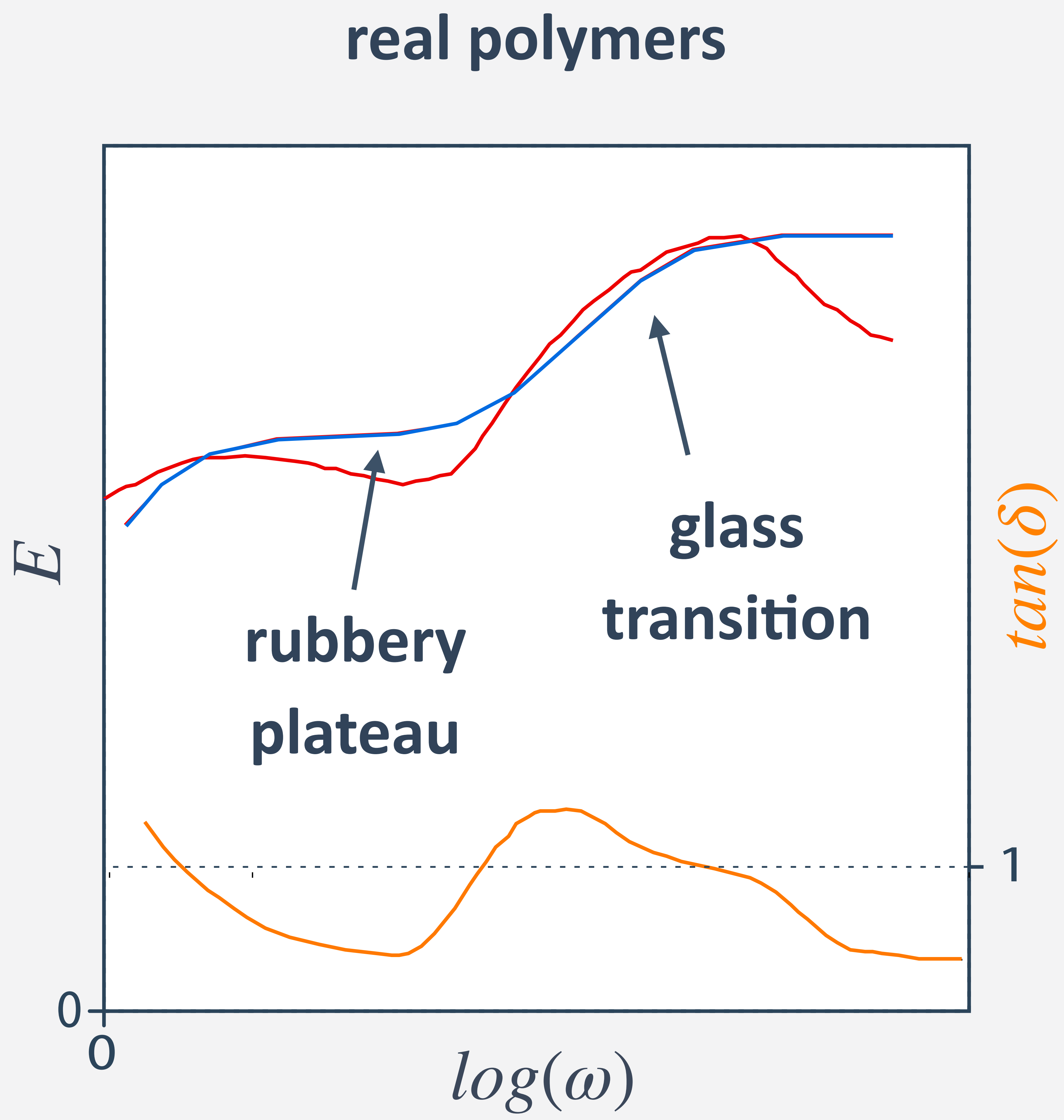
+

MeOH



Limitations

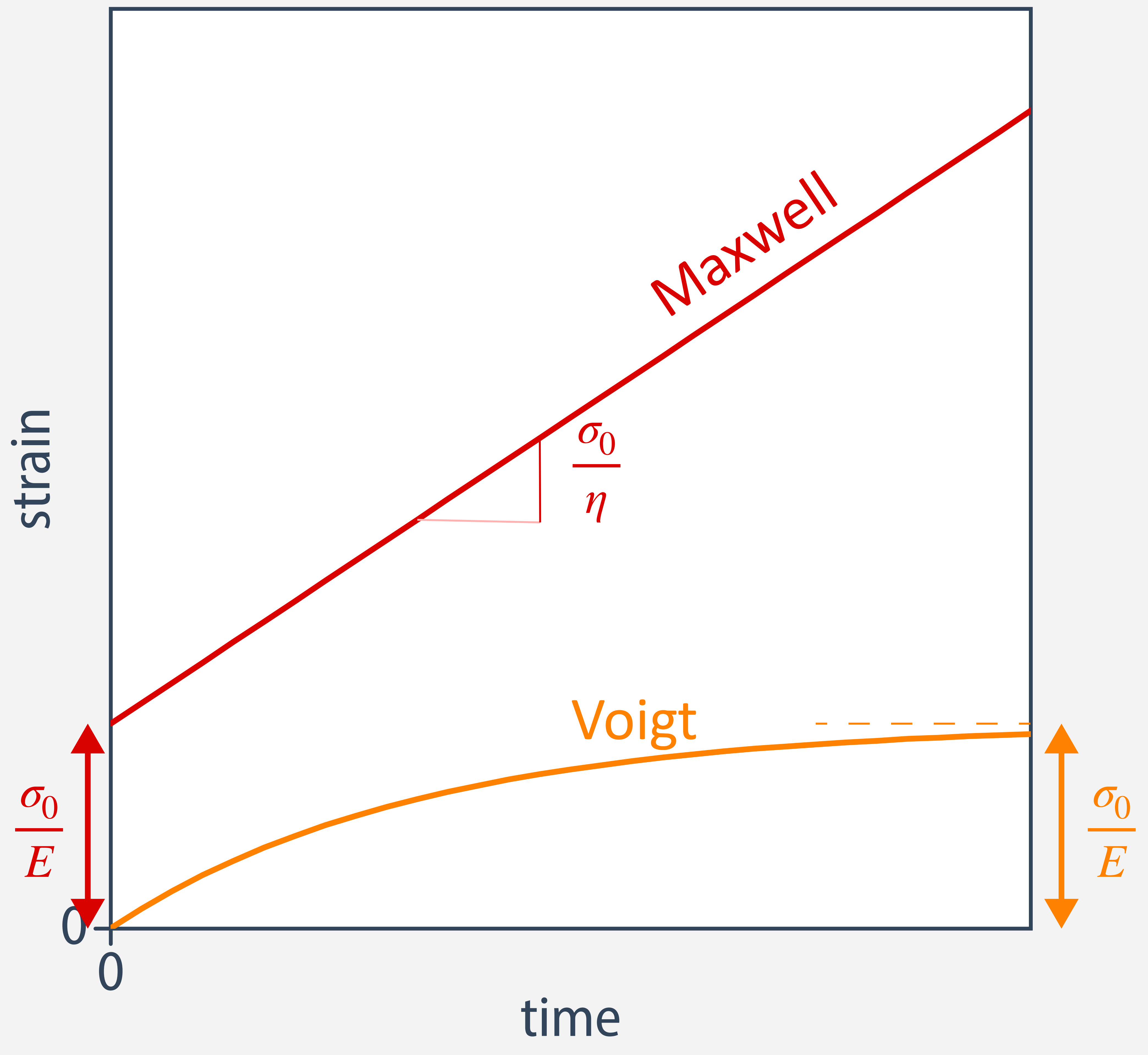




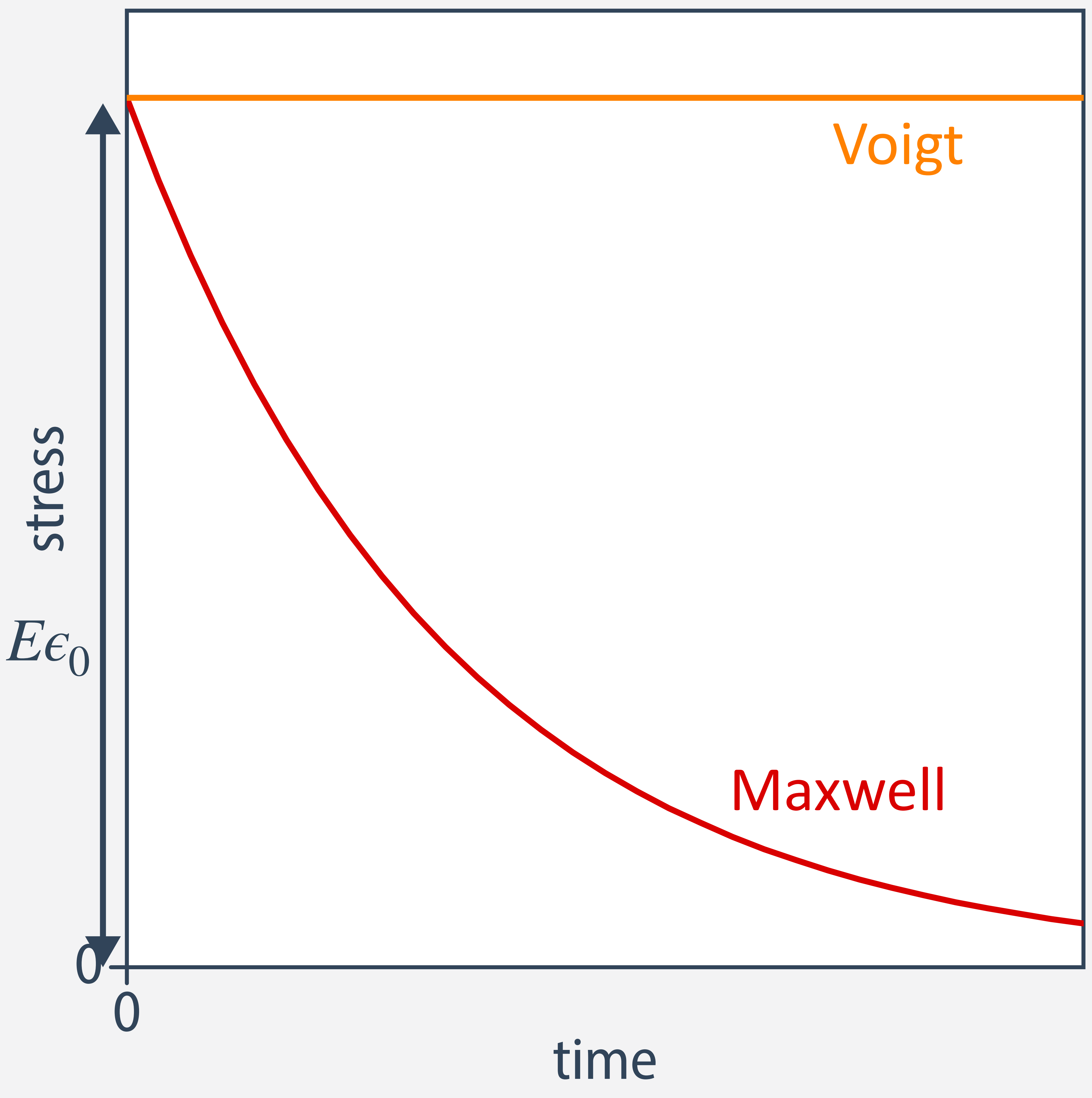
- the Maxwell model is too simple to account for the behaviour of real polymers
- this is also the case for the Voigt model (parallel arrangement of spring and dashpot) (see Exercise)

Maxwell vs. Voigt Model

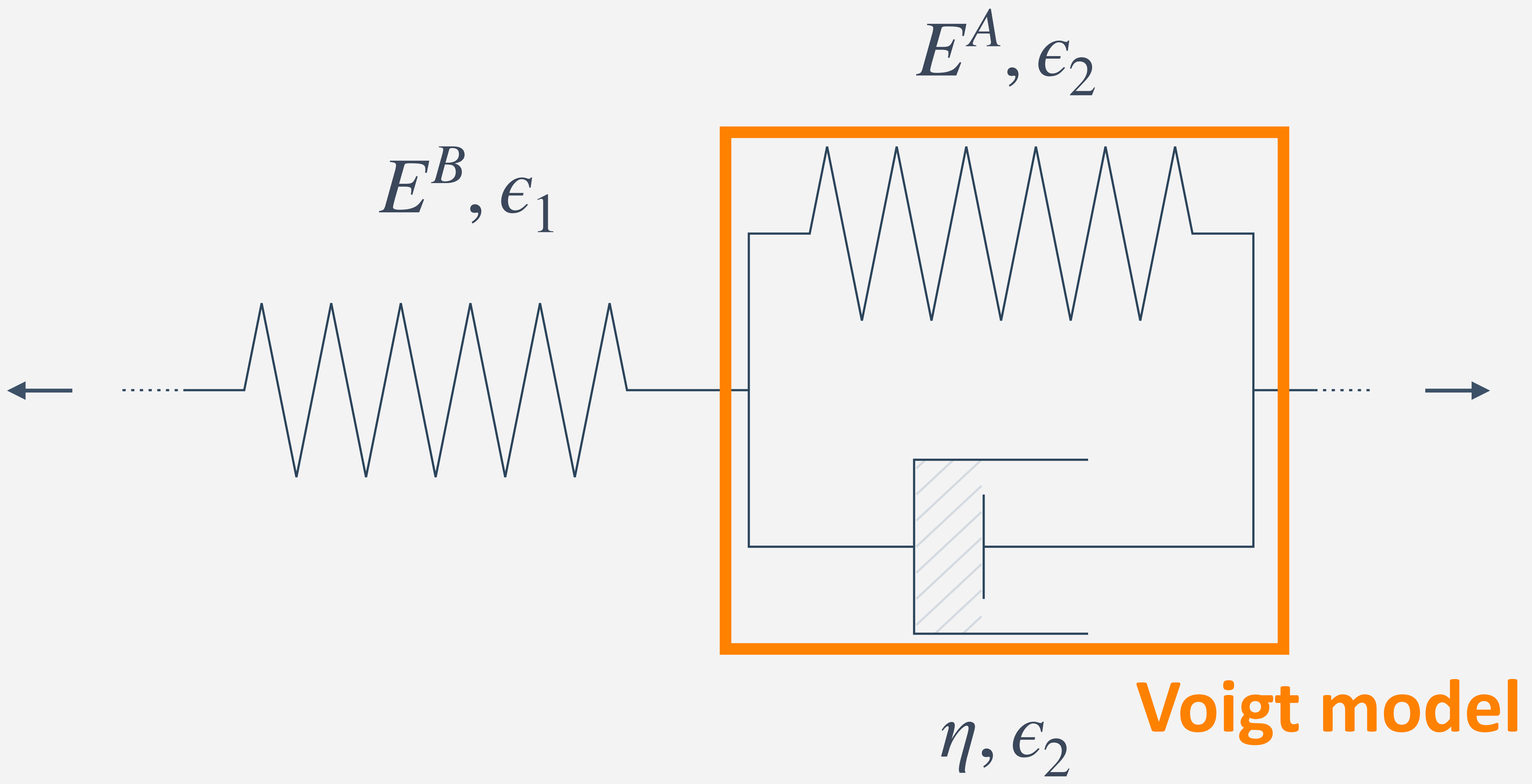
creep experiment
(constant stress σ_0)



relaxation experiment
(constant strain ϵ_0)



- **the Zener model:**



$$\epsilon^* = \epsilon_0 e^{(i\omega t)}$$

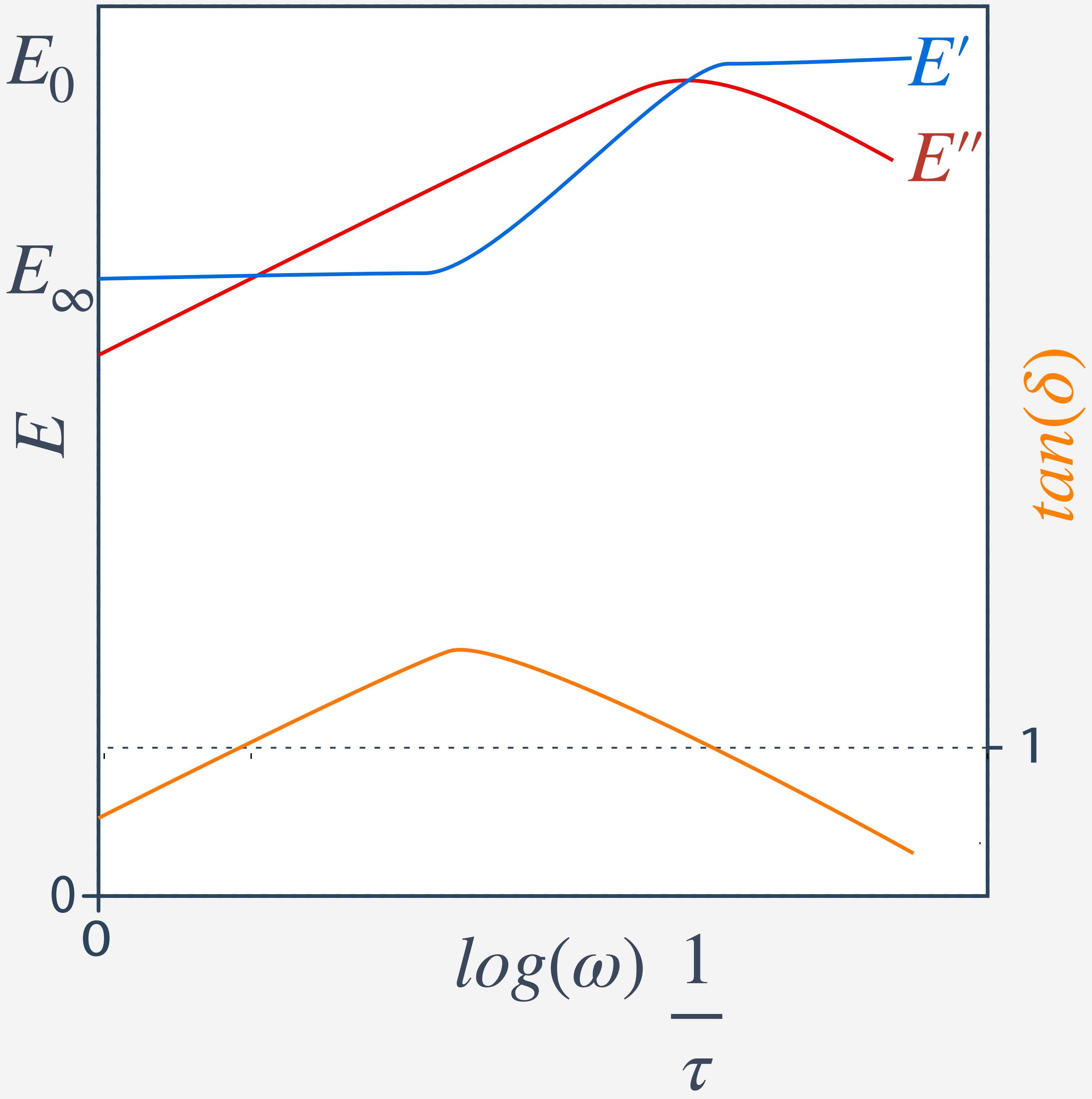
- **we use:** $E_0 = E^B$ $\quad E_\infty = \dfrac{E^A E^B}{E^A + E^B}$ $\quad \tau_\delta = \dfrac{\eta(E_0 - E_\infty)}{E_0^2}$

- **after some calculations, we find:**

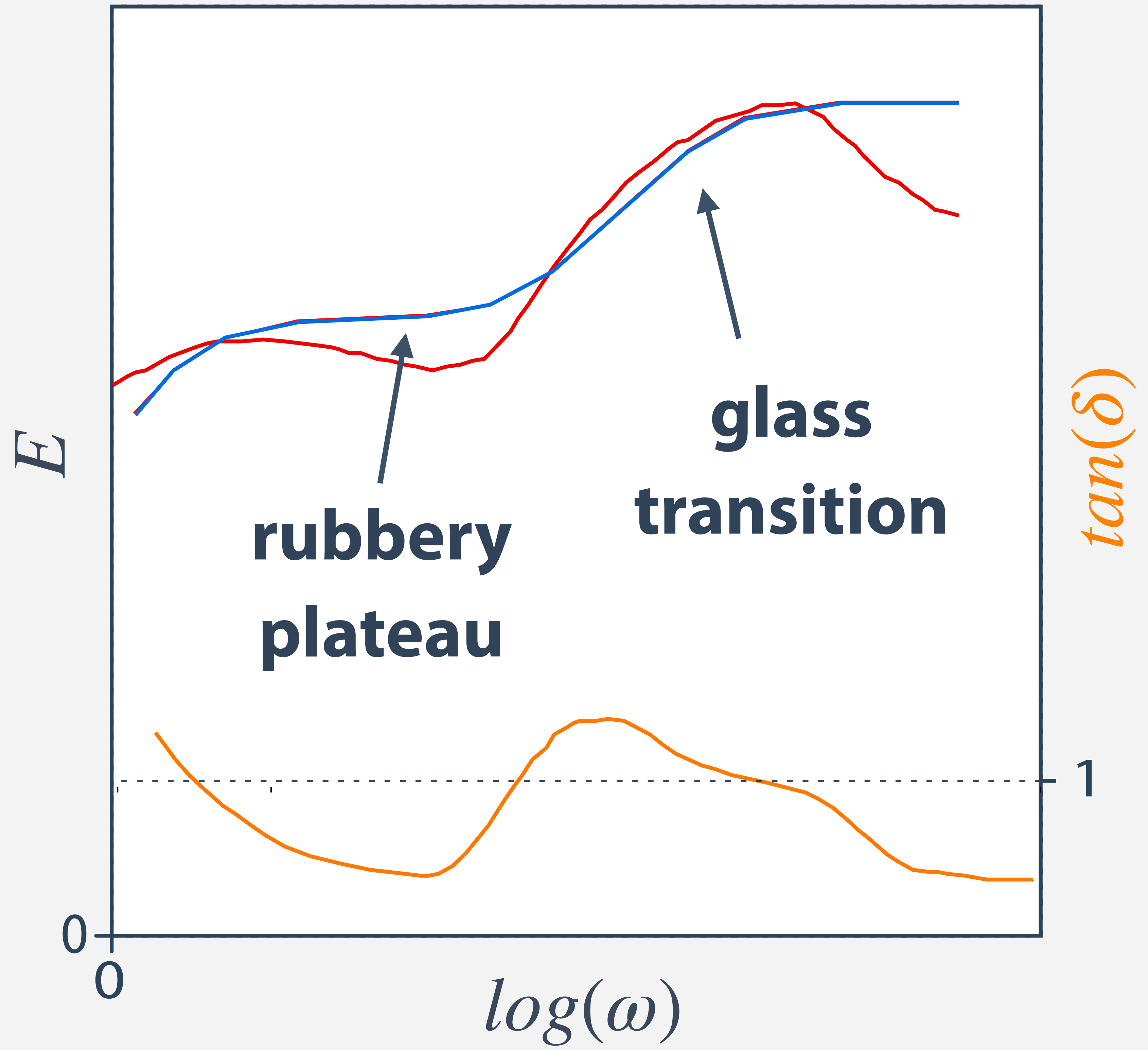
$$E' = E_0 - \frac{E_0 - E_\infty}{1 + (\omega\tau_\delta)^2} \qquad E'' = \omega\tau_\delta \frac{E_0 - E_\infty}{1 + (\omega\tau_\delta)^2} \qquad tan(\delta) = \frac{\omega\tau_\delta(E_0 - E_\infty)}{\sqrt{E_0 E_\infty}(1 + (\omega\tau_\delta)^2)}$$

Basic Mechanical Behavior

Zener model



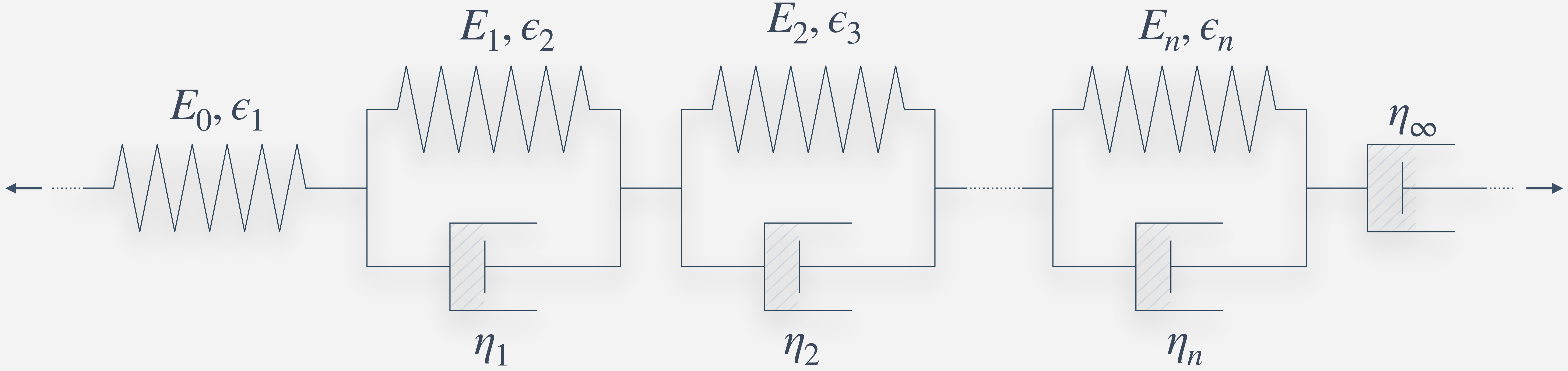
real polymers



- E'' always shows a peak at the glass transition.
- E' tends towards E_0 for $\omega \ll 1/\tau_\delta$ and takes the value of the Maxwell model for $E^A = 0$

Generalised Voigt-Maxwell Model

- **relaxation time distribution based on more accurate models from multiple elements:**



$$E(t) = E_\infty + \sum_1^n E_i e^{(-\frac{t}{\tau_i})}$$

- **for continuous conditions, we get the relation to a relaxation time spectrum $H(\tau)$:**

$$E(t) = E_\infty + \int_{-\infty}^{\infty} H(\tau) e^{-\frac{t}{\tau}} d ln \tau$$

- **Cole-Cole equation as another empirical equation:**

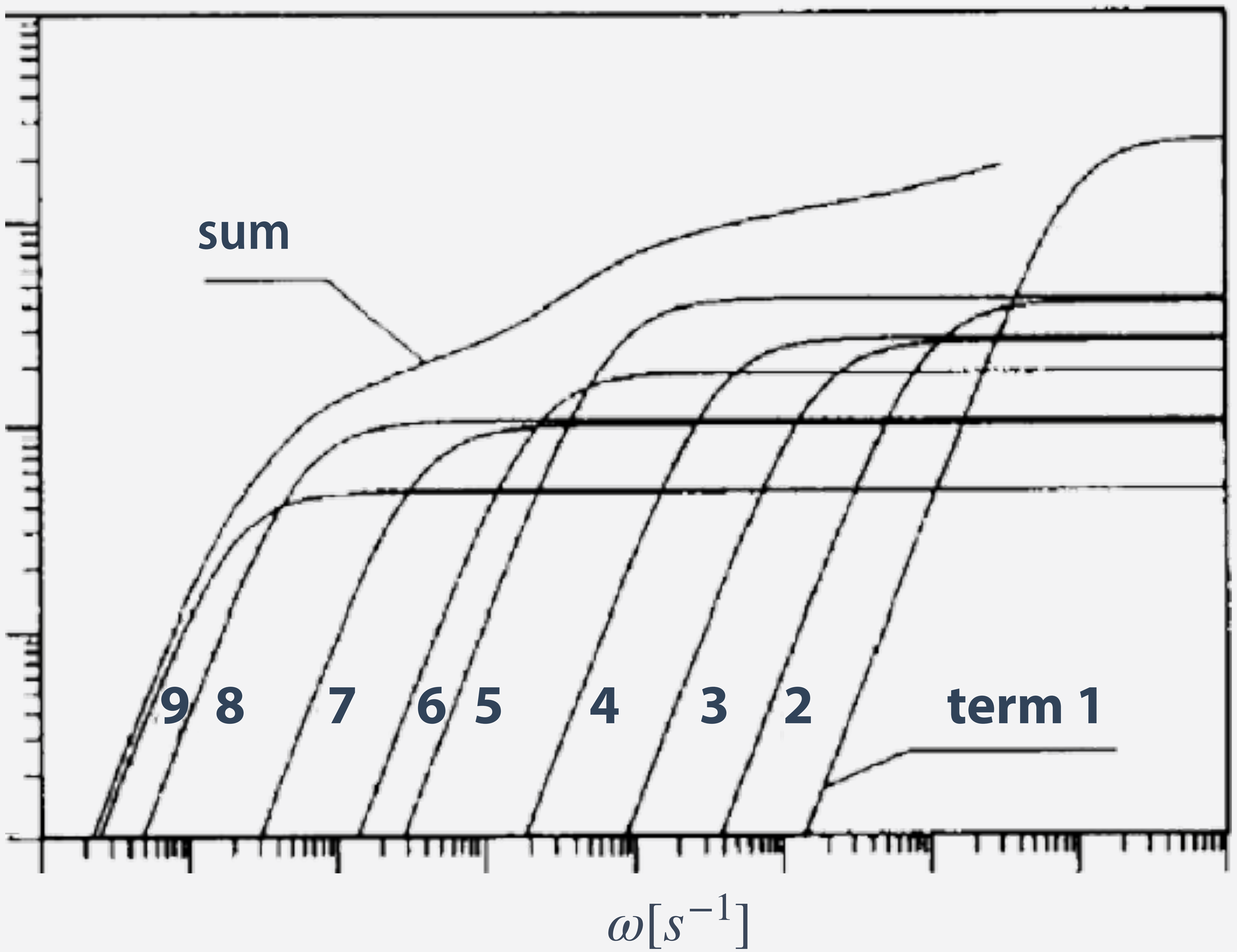
$$\frac{E^* - E_0}{E_\infty - E_0} = \frac{1}{e + (i\omega\tau)^\beta}$$

Generalised Voigt-Maxwell Model for Dynamic Behavior

$$G(t) = \sum_{i=1}^{N} G_i e^{-\frac{t}{\tau_i}}$$

$$G'(t) = \sum_{i=1}^{N} G_i \frac{(\omega\tau_i)^2}{1 + (\omega\tau_i)^2}$$

$$G''(t) = \sum_{i=1}^{N} G_i \frac{\omega\tau_i}{1 + (\omega\tau_i)^2}$$

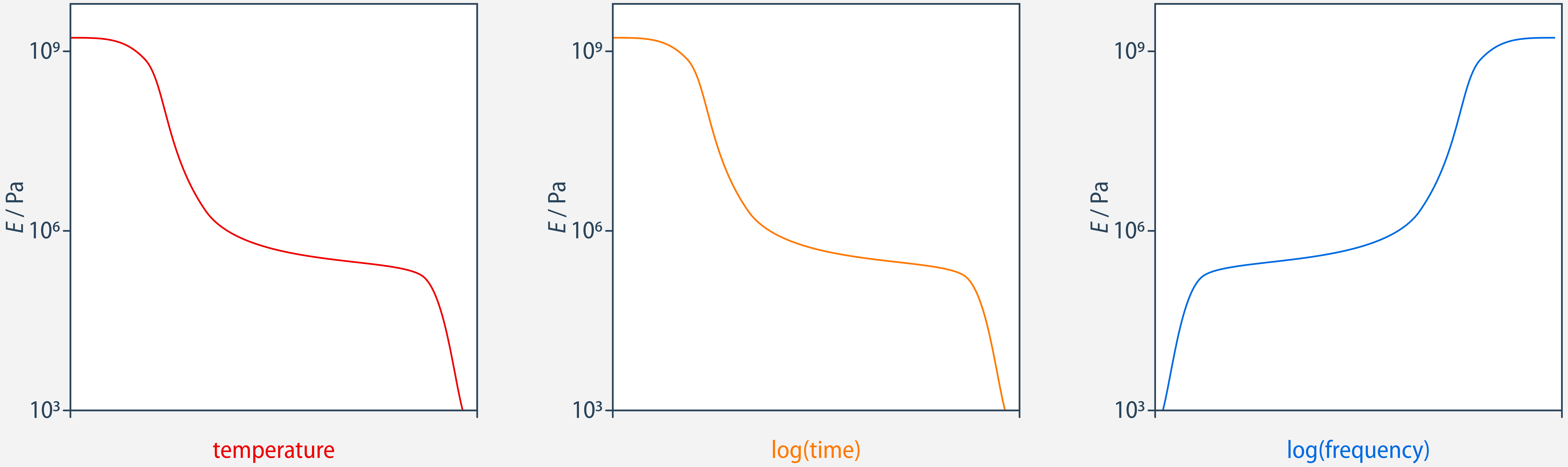


- at the lowest frequency, the behavior is dominated by the longest relaxation time
- G_i and τ are empirical parameters with often unclear physical interpretation

Time-Temperature Equivalence

Time-Temperature Equivalence

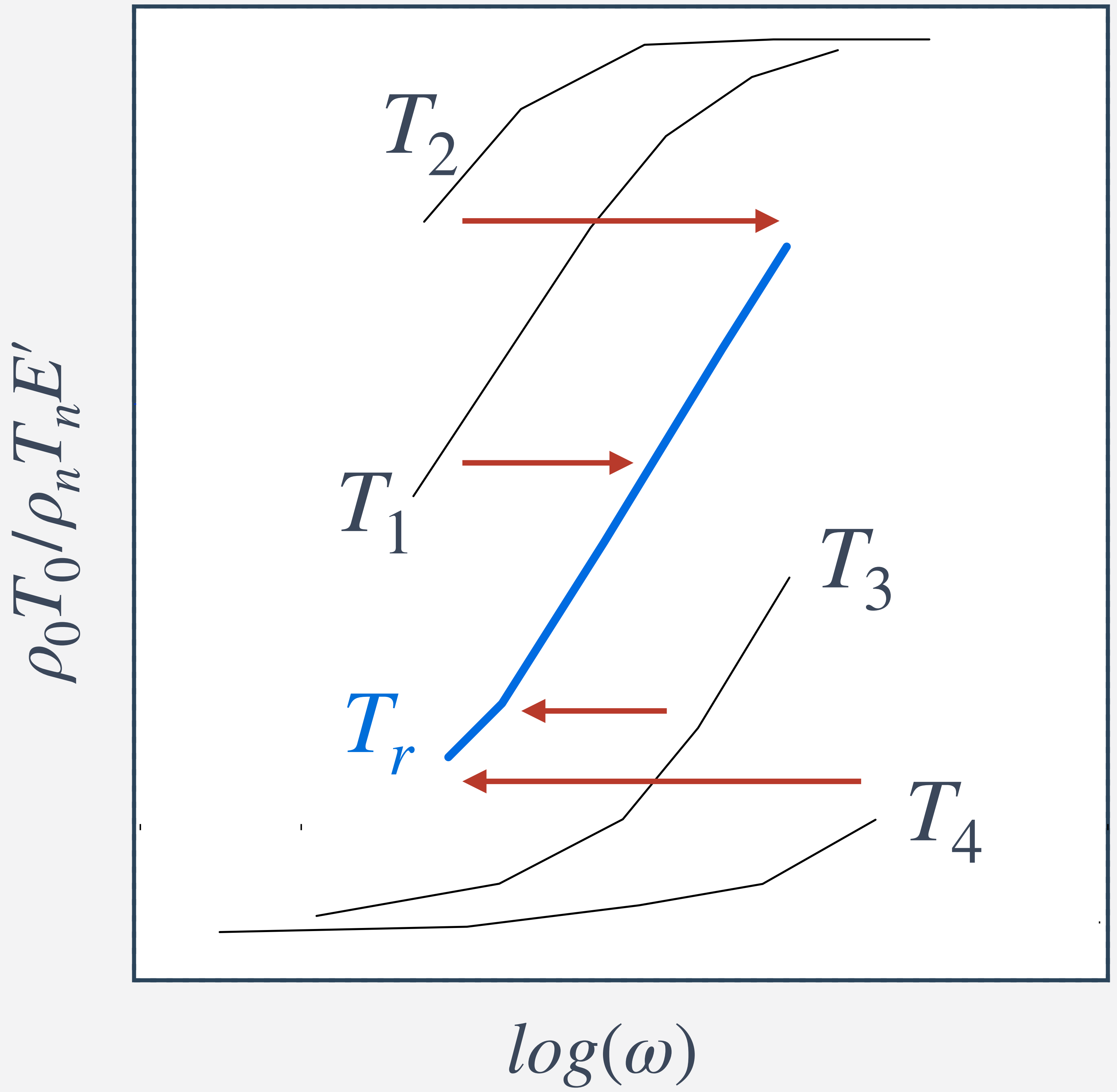
- **qualitatively similar behavior of E, when temperature or time are increased, or frequency is decreased**

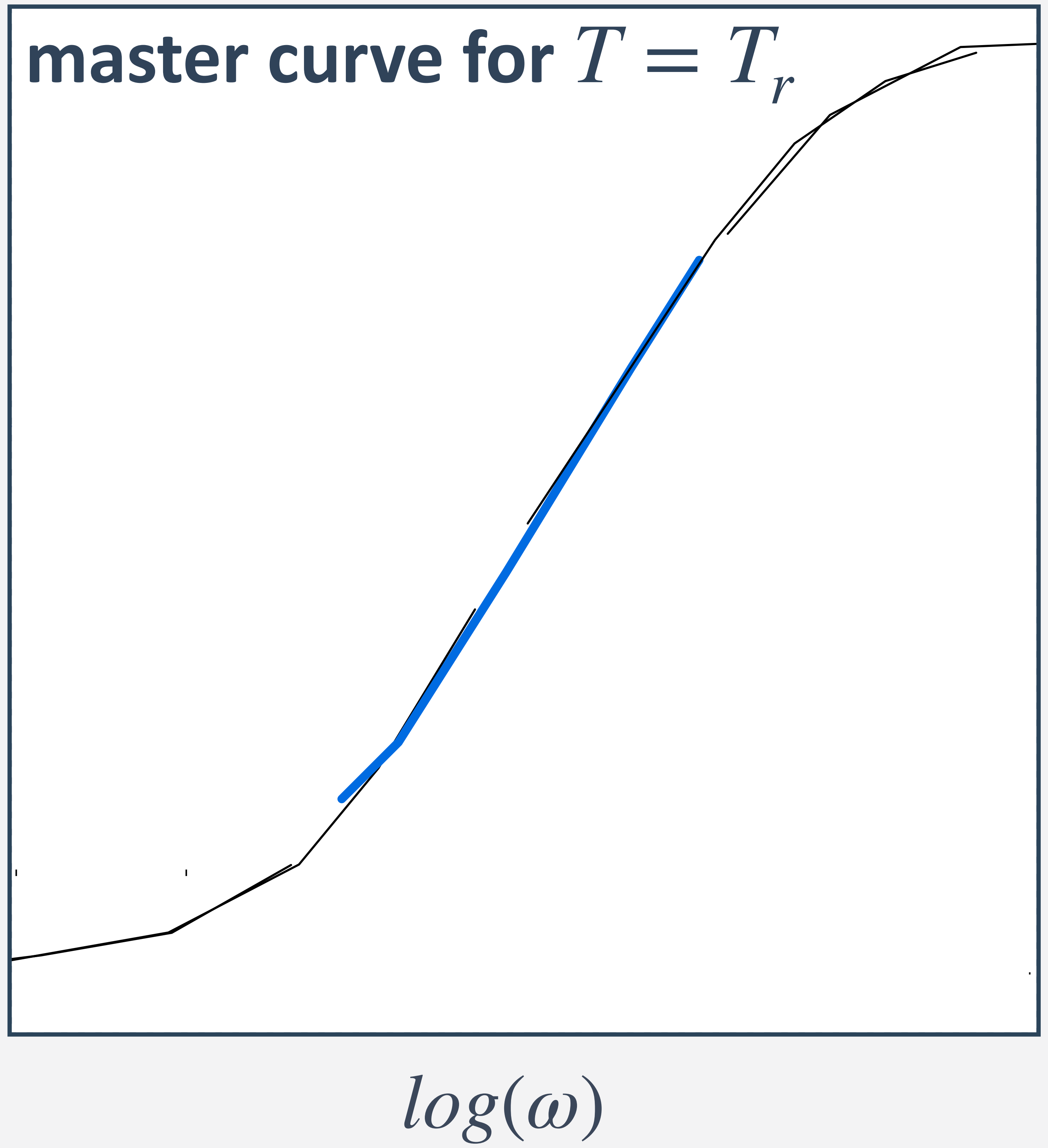


- **is it possible to relate the time (or frequency) and temperature in a more concrete way?**

Time-Temperature Superposition

- measurements of E' as function of frequency at several different temperatures

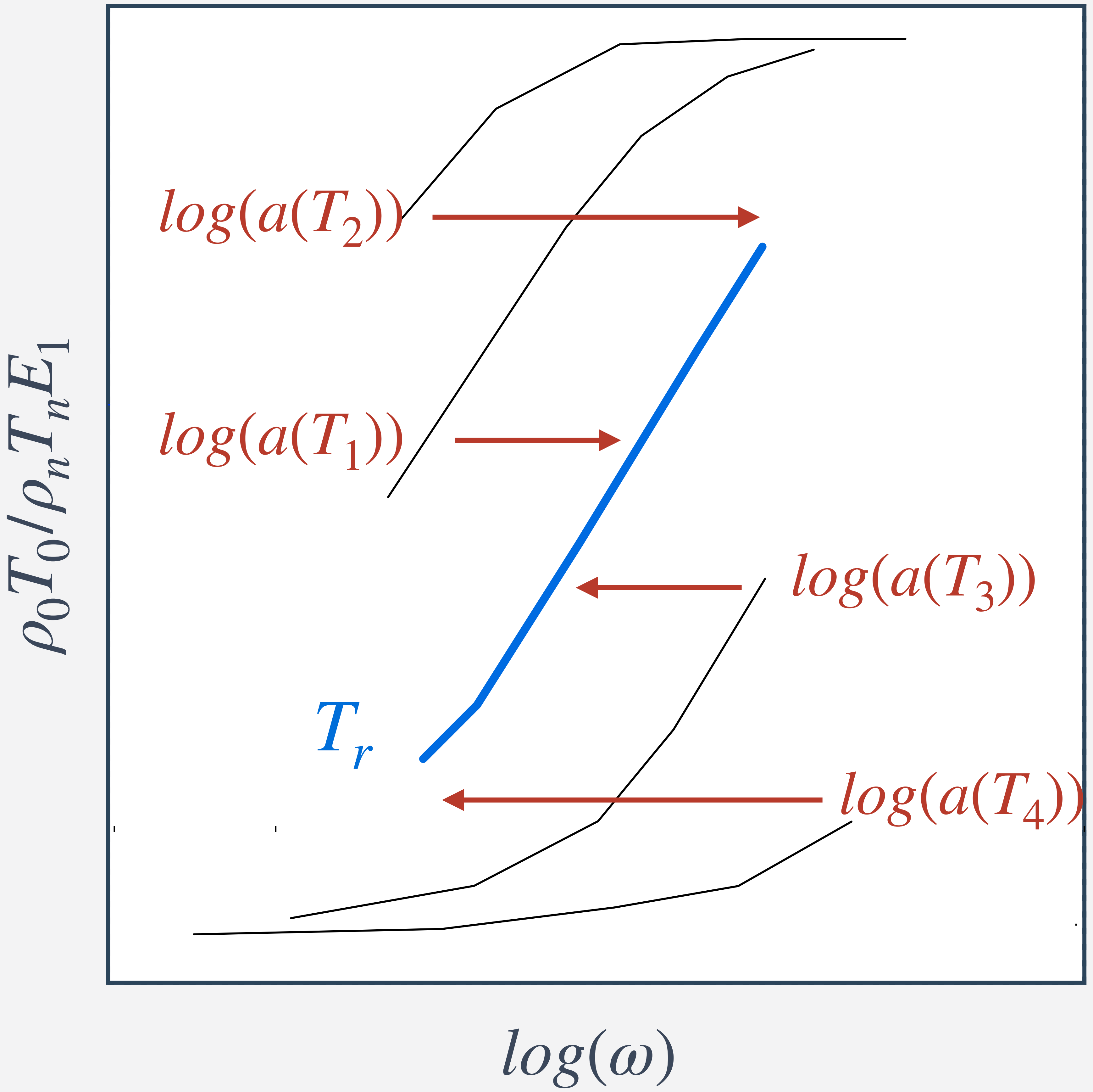




- **after correction for ρT, superimposed data by horizontal displacements along $log(\omega)$ axis**
- **this allows to cover the behavior at frequency ranges that are experimentally inaccessible**

Williams-Landel-Ferry (WLF) Equation

- **the displacement factors follow the empirical WLF equation:**



$$log(a_T) = log(\omega_r) - log(\omega) = log\left(\frac{\omega_r}{\omega}\right)$$

$$\boxed{log(a_T) = -\frac{C_1(T - T_r)}{C_2 + T - T_r}}$$

for $T_r = T_g$:

$$log(a_T) = -\frac{17.44(T - T_r)}{51.6 + T - T_r}$$

- **using T_g as the reference temperature, C_1 and C_2 adopt universal values**

Interpretation by the Free Volume Theory

- assumption: one or more relaxation times at temperatures close to T_g

- free Volume Theory: $\tau(T) = \tau_0 e^{\frac{v_0}{v_f}} = \tau_0 e^{\frac{\Delta\alpha^{-1}}{T - T_0}}$ see **Slide 137**

- let $T_0 = T_g - A$, $\tau(T) = \tau_0 e^{\frac{\Delta\alpha^{-1}}{A + T - T_g}}$, $\tau(T_g) = \tau_0 e^{\frac{\Delta\alpha^{-1}}{A}}$:

- we saw: $a_T = \frac{\omega_{T_g}}{\omega(T)} = \frac{\tau(T)}{\tau(T_g)}$ $\quad ln a_T = ln\tau(T) - ln\tau(T_g) = \frac{\Delta\alpha^{-1}}{A + T - T_g} - \frac{\Delta\alpha^{-1}}{A}$

$$ln a_T = -\frac{A^{-1}\Delta\alpha^{-1}(T - T_g)}{A + T - T_g}$$

compare with the WLF equation: $log(a_T) = -\frac{C_1(T - T_r)}{C_2 + T - T_r}$

Implications and Limitations of the WLF Equation

- the range of frequencies or time accessible by experiments is often limited and can be extended accessed using the WLF approach (very useful to predict creep behavior).

- restricted approximately to a temperature range $T_g < T < T_g + 50\ K$

- often deviations from the “universal” constants

- WLF does not apply to non-linear behavior (large deformations)

- justified only, if it is applicable to all experimental quantities at a time ($E', E'', tan(\delta)$)

Learning Outcome

- polymers are viscoelastic materials, their mechanical behaviour is highly sensitive to the timescale of the measurement.

- linear viscoelasticity may be applied when the deformations are small, allowing the application of simple models for the time dependent behaviour.

- time-temperature equivalence is a qualitative feature of the behaviour of polymeric materials. It is invoked to justify the practice of time-temperature superposition, which can be used to greatly extend the time or frequency range of measurements.